Surface Phases and Processes on Si Surface

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The general observations concerning the commonly accepted terms related to Si surface like ‘surface’, ‘surface phase’, ‘adatoms’, ‘in phase’ and ‘on phase’ atoms are given. Surface phases preparation, composition and their role in surface processes is examined. The influence of surface phases on processing as diffusion, desorption, codeposition, interface formation and surface conductivity is described. [DOI: 10.1380/ejssnt.2004.56]

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I. SURFACE AND SURFACE PHASE

One of the main problems of surface science is the separation of ‘bulk’ and ‘surface’ properties. Success in solution of this problem has much potential for yielding information about different surface phenomena. It can help to answer the questions ‘what happens’ and ‘why it happens’ at the surface. ‘To divide ‘bulk’ and ‘surface’ properties and processes some definitions should be done.

In the classical (‘bulk’) science we have clear definitions of ‘phase’, ‘phase diagram’, etc. Surface science is currently a rapidly developing branch of materials’ science and is still far from the status of ‘classical’ science with its developed system of definitions, concepts, and terminology. So, there are more questions than answers in surface science. Let us consider firstly - what ‘surface’ is?

A. Surface and surface thickness

It is well known that the surface is a boundary between two phases (very often between solid and vacuum). According to Gibbs if Y is some thermodynamic magnitude (free energy, for example) of real solid with surface, y the same thermodynamic magnitude per one ‘bulk’ atom and N - is quantity of all atoms it is possible to write:

\[ Y_S = Y - yN, \]

where yN is thermodynamic magnitude of hypothetical solid with N atoms acting as bulk atoms. Ys related to the difference in this magnitude of the bulk and surface.

In other words (in the case of solid in vacuum) surface is a layer on the top of solid, which has different properties in comparison with the same layer in the bulk. One can find the difference in thermodynamic values or such properties as interatomic distances, crystallographic lattices, electronic structures, and electrical characteristics. Surface thickness can be of a few monolayers (if parameter is ‘interatomic distance’) or thousands layers and more (if parameters are some of electrical properties). Hence, the surface has different thickness for distinct properties depending on the surface phenomena under investigations.

B. Surface phases and thermodynamic equilibrium

This paragraph discusses the term ‘surface phase’. It is well known that atoms at the surface sometimes (not always!) form the periodic two-dimensional structures. Though a large number of publications have been devoted
to the above subjects, it is not safe to say that the term 'surface phase' is commonly used in surface science literature as the definition of these structures. Other terms like 'surface superstructure', 'surface relaxation', 'surface reconstruction', 'two-dimensional (2D) lattice', 'surface structures induced by adsorbate atoms', 'ordered super-lattice', 'ordered adsorbate layer', etc. are also used as synonyms of what we call 'surface phase'. Which term is more correct? What is a physical nature of such structures’ formation? Let us discuss these problems since correct definitions are directly connected with the best understanding of all surface phenomena.

Surface phases: Generally, all processes come to the thermodynamic equilibrium state of the system. Such states of a substance, which can exist simultaneously with each other in the thermodynamic equilibrium while in contact, are phases of the substance. The definition of phases as 'substances in the thermodynamic equilibrium' is well known in the classical ('bulk') physics and can be found, for example, in [1]. The processes on the surface (like those in the bulk) are also directed to the establishment of the thermodynamic equilibrium state of the system.

For closed systems (system with constant energy) 'to reach thermodynamic equilibrium' means to reach the maximum of entropy, i.e. the maximum of disorder. That is a reason why two different gases separated by partition will start to mix (without changing of energy) if to remove this partition. Adsorbates on the surface also can diffuse to the bulk to increase the entropy. But in the solid interaction energy of atoms (or molecules) is high and the energy of system is variable. The processes of adsorbate diffusion to the bulk are directed to reach minimum of free energy \( F \) of all system (substrate with adsorbate) according to Second Law of Thermodynamics

\[
F = U - TS,
\]

where \( U \) is internal energy, which consists of free energy \( F \) and unavailable energy \( TS \). If \( U \ll TS \) (case of non-interacted particles diffusion when they act as gas molecules), decreasing of free energy is a result of increasing of entropy \( S \) and adsorbed atoms can diffuse to the bulk. For another cases (interacted particles) one should calculate the difference in \( \Delta U \) and \( \Delta S \) magnitudes. Very often, foreign atoms can’t diffuse to the bulk due to strong increasing of \( U \) (in the case \( \Delta U \gg T \Delta S \)). In that case minimum of free energy of system (sample with adsorbate) coincide to minimum of free energy of surface and all processes on the surface come to surface phases’ formation.

Surface phases are in the thermodynamic equilibrium both with the bulk and with each other (when more than one surface phase is formed at the surface). One can consider surface phase as an extremely thin layer in the thermodynamic equilibrium state with crystalline substrate (with the layer thickness of the order of monatomic layer) which composition, structure, and properties definitely differ from those of the corresponding planes of bulk substrate and bulk adsorbate, as well as bulk adsorbate compound, if available [2]. In other words, the 'surface phase' is a specific near-surface substance in the thermodynamic equilibrium state with its own characteristics and properties.

It should be mentioned, of course, that the presence of foreign atoms of adsorbate at the surface is not a critical requirement for the formation of surface phase since the near-surface layers of atomically clean substrate planes can form their own surface phases. They have atomic geometry significantly different from those of corresponding planes in the bulk, see for example, structure of Si(111)\(7 \times 7\) surface phase [3].

Other terms show some characteristics or indications of such structures formation and usually are not thermodynamically accurate.

For example, at thermodynamically quasi-equilibrium conditions it is possible to organize on the surface 'two-dimensional lattice' which cannot exist in equilibrium situation. That will be '2D-structure' but not the surface phase.

Term 'surface reconstruction to saturate dangling bonds' is coming from the beginning of surface science. Most likely, Germer was one of the first to consider that substrate atoms can leave their 'bulk' positions and form some kind of 'two-dimensional' compound with adsorbate atoms [4]. It was speculated later that such 'reconstruction' incorporates some quantity of adsorbate atoms (if present) and one monolayer of substrate atoms, which are 'reconstructed'. In that event the reason of 'reconstruction' is assumed to saturate free dangling bonds of topmost Si atoms by forming new bonds, like in the case with Si(111) surface with 1 monolayer (ML) of H [5]. Last case leads to decreasing of the surface free energy to minimum (i.e. surface phase formation occurs).

But, as it was shown relatively recently, the quantity of substrate atoms taking part in the surface phase formation (as well as quantity of adsorbate atoms) can be equal, less or more than one monolayer, see, as example, Fig. 1. On this figure Na atoms (which like H has also valence of one) formed with Si atoms surface phase \( \text{Si}_{x} \text{Na}_{y} \) with \( 0.33 \) ML of Si and \( 0.33 \) ML of Na [6]. In this case saturation of dangling bonds of topmost Si atoms by 1 ML of Na atoms does not lead to minimum of surface free energy. To attain minimum of surface free energy, the formation of new kind of two-dimensional material (surface phase \( \text{Si}_{x} \text{Na}_{y} \)) is necessary. Of cause, in the last case one can use term 'saturation of dangling bonds' also. But strictly speaking we have to say about saturation of bonds of the topmost 'bulk like' Si atoms by 'bonds' of surface phase \( \text{Si}_{x} \text{Na}_{y} \) atoms. It is not so clear and convenient According to traditions, we also term this case as 'reconstruction', though it is clear that the process is more complicate. Term 'relaxation' is usually related to clean substrates. Here substrate atoms just slightly change their own positions.

It is difficult to predict which situation ('relaxation' or 'reconstruction') will proceed exactly. In case of Si we have strong directional local bonding. At presence of directed bonds, breaking of them on the surface usually leads to dramatic effect ('reconstruction') on the atomic rearrangement in the top layers. It is believed that reconstruction process (or surface phase formation) depends on the bonding energies of substrate atoms and adsorbate atoms. One can state with assurance that 'reconstruction' (to suit minimum's free energy requirements) will
FIG. 1: (a) 3D STM presentation of 220×220 Å area on Si(100) surface at initial stage of Si(100)2×3-Na surface phase formation. (b) Structural model for Si(100)2×3-Na surface phase. Silicon atoms are shown as open circles, and sodium atoms are shown as dark circles. The 2×3 unit cell is outlined. From Ref. [6].

occur if

\[ E_A + E_S > E_{AS} + E_i, \]  

(3)

where \( E_A \) is the energy of adsorbate atoms on 'bulk-like' substrate, \( E_S \) is the energy of the top-most substrate 'bulk-like' atomic layer, \( E_{AS} \) is the energy of two-component surface structure after 'reconstruction', and \( E_i \) is interface energy. If two-component surface structure's energy does not fit last equation, or such surface structure simply cannot be formed (for example, due to low temperature), the process of 'reconstruction' does not occur. One would expect that the process of 'relaxation' will proceed.

In the event that surface is free from foreign atoms, the condition for 'reconstruction' is

\[ E_S > E_{SS} + E_i, \]  

(4)

where \( E_{SS} \) is the energy of 'one-component' surface structure after reconstruction.

Term 'surface reconstruction induced by another adsorbate' is also not excellent. Indeed, a lot of different surface atoms' rearrangements are available actually from the fact of presence of certain adsorbate atoms on the surface. This term describes one of the reasons of surface phase formation (existence of another kind of adsorbate at the surface) but not all of them. In fact, the reason is the tendency of system to establish thermodynamic equilibrium. Only one structure is feasible in thermodynamic equilibrium conditions. As we know the equilibrium state of a solid is determined by specifying some two thermodynamic values, for example, concentration and temperature. Thus, for surface phase characterization (and formation) the certain temperature and concentration of both substrate and adsorbate components are necessary. Thus, one can say more correctly that surface phase on silicon is not 'reconstruction' of Si upper layers (since, for example, it could be obtained by deposition of silicon atoms as well) but a new two-dimensional 'construction'.

This is not to say that terms 'reconstruction', 'superstructure' etc. are unusable as definitions of such structures' formation. One important point to remember is that these structures are formed in thermodynamic equilibrium.

'In phase' and 'on phase' atoms: One should distin-
guish foreign and substrate atoms included in the surface phase ('in phase' atoms) and the atoms in excess with respect to the surface phase ('on phase' atoms), see Fig. 2. 'In phase' atoms are relatively strongly bonded with each other. 'On phase' atoms act as adatoms at the surface (surface phase) and weakly bonded with substrate atoms and with each other. This difference is the most important for surface phases' formation and surface processes explanations.

'Adatoms': Term 'adatoms' implies adsorbed atoms on the surface. To keep up the tradition so-called adatoms are any atoms ('in phase' or 'on phase') on the top of substrate. To take one example, according to DAS model of Takayanagi et al. [3] 12 atoms on the top of Si(111)7 × 7 structure are known as 'adatoms' in spite of the fact that these atoms ('in phase' atoms) are constituents of this surface phase.

It should be remembered that some additional amount of 'on phase' silicon atoms deposited onto Si(111)7 × 7 structure (which have absolutely different properties compared to these 12 'adatoms') is also (absolutely correctly) referred to as 'adatoms'. So, we have one term for two dissimilar situations. It is slightly uncomfortable but this is the tradition!

One-component surface phase: The simplest example of such phases is Si(111)7 × 7 on Si substrate etc. This is the example of surface phase formation by 'its own atoms' of the bulk samples.

There are another cases of one-component surface phases' formation. Such phases can be grown due to deposition of adsorbate atoms onto the substrate. Sometimes it happens in the 'classical' (bulk) solid state physics that two substances have a low solubility in each other without forming two-component alloy or solid solution. One can see the same situation in surface physics. In some cases adsorbate atoms after deposition onto the substrate with its own surface phase do not destroy substrate's surface phase. Usually it occurs at low concentration and relatively low temperatures. These adsorbate atoms form a layer of metallic atoms in potential relief of substrate surface phase (for example Si(111)δ − 7 × 7-In, see Fig. 3). This case may be classified as one-component 'adsorbate surface phase on the substrate surface phase'. Let's notice in that case we not deal with two-dimensional one-component surface phase but the system of In nanoclusters, disposed in potential relief of Si(111)7 × 7, i.e. zero-dimensional phase.

The situation is slightly different for Sb deposition onto heated Si(111) substrate. In that case Si(111)7 × 7 surface phase is spoiled but Sb atoms do not mix with Si atoms. 'Bulk' Si atoms preserve their positions [7]. Hence, Si(111)7 × 3-Sb structure is one-component surface phase of Sb on Si substrate.

In above cases both substrate's surface phase Si(111)7 × 7 and bulk phase Si(111) play the role of different 'arenas' for surface phases formation. As a result we could see the occurrence of one-component (zero- or two-dimensional) surface phase (adsorbate surface phase) on the substrate surface phase or on the substrate bulk phase. This term differs from next one ('substrate-adsorbate' surface phase).

It is not obligatory for the 'arena' to be bulk-like Si surface or any of the 'native' surface phases of Si substrate.

It is known that adsorption of many elements may induce a massive rearrangement of Si atoms. Under certain conditions this re-configured Si surface can be used as a new 'arena' resulting in the formation of un-conventional surface phases. One of examples of such behavior is given below.

Sb adsorption onto the clean Si(001)2 × 1 substrate results in the formation of either disordered surface (TS < 550°C) or 2 × 1-Sb surface phase (TS > 550°C) [8]. However, it has been found that the structure of Si(001)-Sb interface can be modified if Sb deposition is performed onto the 4 × 3-In surface phase that is known to has a strongly reconstructed topmost Si layer.

When Sb atoms reach the In-Si surface they displace In atoms destroying In-Si surface. However, if the substrate temperate is low enough (below about 230°C) Sb is unable to ruin the Si sub-reconstruction of this phase. Upon annealing Sb starts to form its own surface phase but the presence of 4\(\sqrt{3}\)-spaced Si dimer chains ('abandoned framework' of the initial 4 × 3-In surface) suppresses the
FIG. 4: STM images of the mixed \((8 \times 2) + (4 \times 2)\)-Sb surface phase prepared by 1 ML Sb adsorption onto \(4 \times 3\)-In surface at RT following by annealing at about 250°C. From Ref. [10].

formation of conventional \(2 \times 1\)-Sb. Instead, the formation of a new Sb-Si(001) surface phase was observed [9, 10] accompanying with desorption and partial agglomeration of In. Fig. 4 shows STM images of this surface phase. It appears as a complex system of double rows with \((8 \times 2)\) and \((4 \times 2)\) primary periodicities. Indium does not make up a part of this structure directly. Nevertheless, In atoms act as a catalyst providing the formation of Sb-Si chemical bonds at low temperature and prepare the Si ‘playground’ for the further formation of mixed \((8 \times 2) + (4 \times 2)\)-Sb phase.

This surface phase is metastable; above about 280°C it dissociates resulting in the restoration of Si bulk-like geometry that allows Sb to form the conventional \(2 \times 1\) surface.

Two-component surface phases. Composition. Identification of surface phase up to date. The composition of two-component bulk phases usually is well known and is written as \(A_xB_y\). Generally we have to write the same for two-component surface phases consist of adsorbate and substrate atoms (‘substrate-adsorbate’ surface phases), see Fig. 2a. One should determine either concentration of ‘in phase’ atoms constituting the surface phase (adsorbate atoms as well as substrate ones). The previous term for surface phase identification (‘adsorbate coverage’) was used in surface physics before understanding that surface phases can be formed by both adsorbate and substrate atoms with their own concentrations. The problem today is the determination of quantity of adsorbate and substrate atoms, but sometimes it is already possible to do. For example, it is known that Si(100)\(4 \times 3\)-In surface phase consists of 0.5 ML Si and 0.6 ML In [11]. Thus, composition of this surface phase is \(Si_{0.5}In_{0.6}\). Such formulas are important for understanding of surface phases physical properties.

It is necessary to stress that substrate surface in the above example is usually not only ‘arena’ which defines surface phase parameters but the source of ‘in phase’ substrate atoms also. Crystallographic structures of these surface phases are determined by interactions between adsorbate atoms with each other, adsorbate atoms with substrate atoms, as well as substrate atoms with each other.

Unfortunately, concentrations of surface phase’s components are usually unknown. On the other hand, among other characteristics, the crystallographic structure is believed to be the most fundamental one for the identification of certain phase. It was the reason why the surface phases till to now are usually labeled in accordance with their periodicity with respect to the underlying substrate crystal plane (see, for example, indication of surface phases on Si [2]).

Three-component surface phase. Presence of two kinds of foreign atoms on the monocrystalline substrate sometimes leads to the new type of three-component surface phase formation, see Fig. 2b. Simple reasoning concerning the determination of two-component surface phases’ composition is appropriate for three-component surface phases.

Single-crystalline and polycrystalline surface phases. Defects of surface phase growth. A tendency of surface atoms ‘to organize’ system with minimum of free energy leads to new substance growth with its own crystallographic structure and composition. One can say that the new substance is epitaxially grown on single-crystal substrate. Adsorbate and substrate atoms ‘select’ the ‘best’ lattices, compositions and orientations on a substrate surface. Sometimes (very seldom) this ‘selection’ is impossible and epitaxial surface phase cannot be formed (for example, N with Si form on Si(111) substrate surface phase Si(111)-8 \(\times \) 8-N but O and Si does not form ordered surface phase on Si(111)).

Surface phases can be both single-crystalline and polycrystalline. Polycrystalline structure formation gives rise to some growth defects. Let us explain these terms by analogy with ‘bulk’ physics.

Bulk crystals have two-dimensional defects, which are spoken of as dislocations. A surface has such own defects of a similar nature as dislocations (which formed as a result of three-dimensional polycrystal growth). These surface defects occur when several (two or more) two-dimensional islands of ordered surface phases start to grow in the several azimuth orientations and then contact...
FIG. 5: Two-dimensional polycrystal: a) in the first stage of polycrystalline surface phase formation (scheme); b) final stage (scheme); c) STM image of two-dimensional polycrystal (by courtesy of Prof. A. A. Saranin).

FIG. 6: Scheme of polycrystalline (multi-domain) surface phase growth as a result of competition of 3D- and 2D- epitaxy. Areas ‘1’ and ‘2’ related to the ordered surface phases formation with different azimuth orientation.

with each other, see Fig. 5.

So, the surface that contains domains of a given phase in different orientations might be considered as a ‘polycrystalline’ surface phase, while the surface of one phase in a single orientation might be considered as a two-dimensional analog of a single crystal. It seems evident that the distinction between the polycrystalline phase and the disordered phase is to a great extent a matter of convenience depending on the critical domain size.

Surface phases crystallinity is a function of experimental conditions of such kind of epitaxy and depends on the competition of two epitaxial rates (Fig. 6). The first epitaxial rate ‘$V_{3D}$’ characterizes epitaxial process from bulk side perpendicular to the surface. The second one (‘$V_{2D}$’) relates to 2D-epitaxy on the source side of the surface phase (which has already grown) along the surface. The similar situation we can observe also for ‘bulk’ epitaxy. For example, the formation of monocrystalline layer during solid phase epitaxy depends on growth rates ratio of epitaxial layer from interface of amorphous film-monocrystal and on rate of size increasing of crystalline nuclei.

Electronic structure. Let us consider the term ‘electronic structure of surface phases’ using the formation of electronic structure in bulk phase of Si as an example. Suppose that bulk Si has some admixture (for example, doping atoms), which give discrete electronic levels to the forbidden gap. Increasing of the doping atoms concentration leads to new bulk phase formation that is known as silicide with its own valence band. Such valence band considerably differs from those of the bulk silicite.

C. Surface phases formations

It has already mentioned that thermodynamic equilibrium conditions are necessary for surface phases formation. Recall that the values fundamental to this kind of experimental procedure are concentration and temperature. Thus, a way of delivering of foreign atoms and substrate atoms onto the surface is not important for surface phase formation. Let us consider the experimentally accessible occurrence of surface phases.

Deposition onto heated substrate. This method is widely met in practice. The best results could be obtained at the substrate temperature $T_s$, which is lower than the temperature $T_b$ of the breaking bonds in the ‘substrate-adsorbate’ surface phase, but higher than the temperature $T_d$ of foreign ‘on phase’ atoms desorption. Deposition of foreign atoms at the temperature range $T_s < T_b$ leads to the surface phase ‘substrate atoms-adsorbate’ formation. Next portion of deposited foreign atoms will act as ‘on phase’ atoms, which are weakly bonded with substrate and leave the surface at the growth temperature used ($T_d < T_s < T_b$). When $T_d > T_s$, some adsorbate atoms remain on the surface as ‘on phase’ atoms. These atoms diffuse easily along the surface and form clusters or islands. The size and density of islands are functions of the amount of ‘on phase’ adsorbate atoms, temperature, substrate and surface phase properties.

One can say that the above procedure (deposition at high temperature and oriented 2D-structure growth) is a kind of Molecular Beam Epitaxy (MBE). The crystallinity of such grown surface phases depends on deposition rate of adsorbate, diffusion coefficient of adsorbate atoms on the substrate, competition of 3D- and 2D-epitaxy, and other experimental conditions.

Room temperature (RT) deposition and annealing. As this takes place we are frequently dealing with the amount of foreign atoms in excess to the concentration of ‘in phase’ atoms in ordered surface phase. After RT deposition, during annealing at middle temperatures for surface phase formation (see Fig. 7), some ‘on phase’
foreign atoms remain on the substrate (usually they are free to move along the surface and form islands). ‘On phase’ atoms behavior depends on substrate temperature, amount of adsorbate, diffusion coefficient, substrate and adsorbate properties.

We are entitled to call this method of ordered surface phases formation (when adsorbate is deposited at relatively low temperatures with further annealing) as Solid Phase Epitaxy (SPE). The crystallinity of resulting surface phases is not quite good. One should repeat that it depends on the competition of ‘2D’- and ‘3D’- epitaxial rates.

Surface phase preparation due to diffusion. Diffusion process for surface phase formation is convenient to form several ‘adsorbate-substrate’ surface phases with variable compositions. This method makes it possible to test different kinds of surface phases in the same experimental conditions. Beyond that point, it can be used for single-domain (monocrystalline) surface phase formation, see Fig. 8. One should point out that properties of monocrystalline surface phase are essentially differs from polycrystalline ones. Such is the case for surface phase conductivity of single-domain and polycrystalline Si(111)\(5 \times 2\)-Au [12].

Let us describe the most popular experimental procedure. First, one should deposit an adsorbate strip with several monolayers thickness onto the substrate at RT. Then, as a result of annealing, adsorbate atoms diffuse onto the clean substrate and form different surface phases according to the adsorbate concentration. Since adsorbate atoms diffuse from ordered surface phase side, monocrystalline surface phase growth occurs only as a result of ‘2D’-epitaxy, see Fig. 8a.

Annealing of highly doped substrates. This method is an interesting example of the exotic way of foreign atoms delivering onto the surface, in which foreign atoms come to the surface from bulk side. As we know already, the result must be identical to that for the same amount of foreign atoms’ deposition. Such experimental procedure was realized on the highly B doped Si(111) sample [13]. During annealing, Si atoms desorbed from the substrate and B atoms remain on the surface, since Si-B atomic binding energy is essentially higher than Si-Si one, see Fig. 9. Accumulation of B atoms leads to Si(111)\(\sqrt{3} \times \sqrt{3}\)-B surface phase formation. This type of surface phase formation is not quite common. We know just one example of such procedure described above. It is presented here to underline once again the need for certain concentration and temperature in order to form surface phase. The way of delivering both kinds of atoms (adsorbate atoms and substrate ones) is not important.

Deposition of substrate and adsorbate atoms. Deposition of adsorbate atoms on Si substrate usually only is used for ‘silicon-adsorbate’ surface phase formation. This is related to the fact that Si substrate acts not only as arena but source of Si atoms as well. Often it leads to surface roughness formation since some surface phase can included not whole number of Si atoms [14]. Predeposition of appropriate amount of Si atoms on Si substrate (which are necessary for stoichiometric compo-
FIG. 9: Increasing of B surface concentration during annealing: a) scheme of B accumulation; b) concentration changing of B atoms during annealing; c) LEED structure of Si(111)√3×√3-B surface phase. From Ref. [13].

Disruption of surface phases. Existence of any surface phase is characterized by certain range of temperatures and concentrations. Thus, in order for destruction process to happen, temperature or concentration (or both of them) should be taken outside of this range. The disruption of surface phases occurs in perfect analogy to the bulk phases. In the case of bulk phases the usual ways of disruption are melting (variations in temperature) and variation of ‘bulk’ components’ concentration (for example, by ion implantation). For surface phase to be destructed surface melting (variations in temperature) and adsorption or desorption (variations in concentration) are mainly used.

D. Surface phase diagrams and their construction.

Phase transitions

In the classic (‘bulk’ solid state physics) as well as in the surface state physics we must constantly keep in mind that these systems (bulk and surface) have a very large number of atoms (∼10^23 cm^-3 and ∼10^15 cm^-2 respectively). Thus, macroscopic characteristics of large surface subjects can be obtain from the same thermodynamic laws, which are well known in the classical physics.

Among these characteristics, concentration and temperature ranges of different surface phases’ existence are the most important. ‘Surface phase diagrams’ describe surface phases coexistence. The transformation of one surface phase to another is termed ‘surface phase transition’.

As we have already mentioned, measuring concentrations of substrate atoms constituting the surface phase with adsorbate atoms has always been a problem. This is a reason to present a surface phase diagram formation built in the ‘adsorbate coverage temperature’ coordinates, like the schematic one shown in Fig. 11. Such diagrams are not exactly correct (since substrate atoms coverage is also necessary) but every so often useful for surface processes explanations.

The phase diagrams construction can be determined in several kinds of experiments [11]. First, the adsorbate can be deposit onto the Si substrate held at a fixed temperature. After each deposition step, the surface crystallographic structure is elucidated (usually, from the observation of low energy electron diffraction (LEED) or reflection high energy electron diffraction (RHEED) patterns). The set of experimental dots in such a measurement occupies the pass A on Fig. 11. This procedure if repeated at different temperatures provides the possibility for the determination of coverage and temperature ranges at which certain surface phase exists. The graphic presentation
of these data produces the required formation phase diagram.

Second, the adsorbate film of a fixed coverage can be formed at room temperature and then annealed at progressively higher temperatures. In this case, the LEED (RHEED) patterns are recorded and indexed after each annealing step (see path B on Fig. 11). Annealing at high temperatures might result in the noticeable desorption of the adsorbate atoms from the surface and the actual pass (marked as B') should deviate from the vertical pass B towards the lower coverage. So, it is essential to distinguish between the case when the 'coverage' axis shows the adsorbate coverage of a RT deposit before annealing (e.g. determined by means of a quartz crystal thickness monitor) and the case when the coverage of adsorbate left at the surface after annealing (e.g. determined by means of AES) is shown. In the latter case, the experiment might involve the RT deposition of a 'thick' film followed by annealing to cause the isothermal desorption of adsorbate. It is obvious that the corresponding pass (marked by C) is opposite to the pass A.

Essential remark is as follows:

(a) In most investigations, before the LEED (RHEED) observations the heating is interrupted and the sample is cooled to room temperature. However, sometimes LEED (RHEED) observations are performed with the 'hot' sample.

(b) Unfortunately these 'phase diagrams' show LEED (RHEED) transformations only. It is necessary keep in mind that actual phase diagrams have to show stoichiometric composition of surface phases, regions of surface phases solubility, regions of surface phases homogeneity, regions of two surface phases existence etc.

(c) It is well known that Si(111)7×7 structure is stable at lower temperature but one can see Si(111) 1×1 LEED pattern transformation at about 860°C. Such kind of transformation is qualified very often as 7×7 to 1×1 surface transition. It is necessary to note that in this case we deal with 7×7 order disorder transition (some kind of melting [16]), while LEED shows a 1×1 diffraction pattern suggesting an ideal bulk-terminated sample (see, for example, [17]).

Phase transitions can occur due to changing of concentration or temperature singly or together. The ability to detect the reversible phase transformations (or phase transitions) on the surface upon heating/cooling and adsorption/desorption of foreign atoms is unique to this kind of experiment. For two-component surface phase similar transitions can be observed only if foreign atoms remain on the surface (as 'in phase' or 'on phase' atoms). First-order transitions occur at heat evolution, melting, adsorption, evaporation, and transitions between structures with different crystallographic modifications. The sharp reordering of the crystallographic structure can be fixed at transition between surface phases with different symmetries. Second-order transitions related to cases when one phase transfers to a second phase continuously and the competing phases are indistinguishable at the transition temperature.

II. SURFACE DIFFUSION AND SURFACE PHASE FORMATION

This chapter is devoted to the description of surface diffusion on Si surface. Namely surface self- and heterodiffusion are essential for a lot of phenomena, such as homoeptaxy, heteroeptaxy, interface formation, segregation, surface modification, nanostructures’ fabrication, sintering technology, etc. About one-fifth of recent papers in the journal of Surface Science are concerned with surface diffusion [18]. The most attention in this Chapter has been concentrated on the role of surface phases formation in surface diffusion processes.

Often we deal with surface of solids in the thermodynamically nonequilibrium states. An excess of free energy characterizes these surfaces. Examples of such surfaces are crystal surface with some defects, surface of unusual shape; crystal surfaces consist of A-type atoms with different concentration along the substrate surface, which consist of B atoms, etc. In such systems the excess of free energy can be liberated very often as a result of diffusion processes or mass (substance) transport which always tend to reach thermodynamic equilibrium in the system. Thus, diffusion processes on the surface (if we deal with 'ideal' surface without morphological defects) are directed to surface phases formation. It is not to be supposed that diffusion does not occur in the 'equilibrium' crystals, which are free from any irregularities. (Of course, we mean 'irregularities' presence of which leads to the increasing of the free energy of crystal). Atomic migration in 'equilibrium' crystals is due to fluctuation of energy.
A. Some diffusion terms

Let us begin from descriptions of different kinds of surface diffusion existing in literature in which we’ll need later.

Surface mass transfer - surface diffusion, where the surface releases mobile atoms as the temperature increases.

Surface self-diffusion - migration of own atoms on the surface (surface diffusion).

Surface heterodiffusion - migration of A-type atoms (atoms of substance A) on substance B.

Surface goal-directed diffusion - diffusion process directed to eliminate any nonequilibrium situation on crystal surfaces.

Aimless surface diffusion - diffusion of surface atoms without decreasing of crystal’s free energy. Such diffusion process is possible even in ‘equilibrium’ crystals. This type of diffusion often terms as tracer diffusion for surface migration.

Tracer surface diffusion - type of adatoms migration in the absence of a chemical potential gradient and an interaction between diffusing particles. This kind of diffusion can be realized when adatoms density is rather small (for example, about 0.05 ML and less). Such migration process of individual atoms on the surface arena occurs without surface reconstruction. A substrate is considered as a static participant, which has a frozen potential energy landscape.

Chemical (collective) surface diffusion is diffusion of interacting atoms in the presence of a chemical potential gradient. Interaction of adatoms with each others (and with substrate atoms) initiates the decreasing of surface free energy and formation of new 2D-surface phase (when the concentration of diffusing atoms and temperature is sufficient to surface phase transition).

B. The physical reasons of surface diffusion. Diffusion in 'nonequilibrium' and 'equilibrium' crystals

All diffusion processes arise spontaneously and tend to reach thermodynamic equilibrium on the nonequilibrium crystal surfaces or occur as ‘aimless’ diffusion on the equilibrium situation. In this paragraph we discussed situation with nonequilibrium crystal surface. Clear analogy to explain such diffusion process was proposed by Gegusin et al. [19]. He said that typical example of nonequilibrium system is a mountain with stones on the top. Stones have some excess energy which can be released when stones slide roll downhill like atoms diffuse in the nonequilibrium crystals to reach ‘equilibrium’ situation.

In what follows we discuss examples of experimental investigation in which an adsorbate is deposited on some portion of the surface to yield a sharp initial concentration profile. Then this profile is allowed to broaden diffusively. One should note, that profile evolution technique measures only the chemical diffusivity for heterodiffusion, but can do so very directly with a minimum of complicated mathematical modeling.

Let us start from a small amount of adsorbate atoms on clean surface (tracer diffusion).

![Diffusion mechanisms for single adatoms](http://www.sssj.org/ejssnt)

**FIG. 12**: Two-dimensional (a) and three-dimensional gas (b), scheme.

**Diffusion mechanisms for single adatoms.** Tracer diffusion is the simplest type of surface atomic migration. The initial simple model of this surface diffusion was proposed by Frenkel [20]. He employed the image of 'two-dimensional gas' (Fig. 12a) by analogy with usual ‘three-dimensional gas’, see Fig. 12b. 'Two-dimensional gas' is a totality of non-interacted adatoms (foreign atoms or substrate’s ones), which are in chaotic motion on the surface.

Surface steps (Fig. 12a) play a similar role in the gas motion as the surface plane (Fig. 12b). To be involved in surface migration, adatoms have to appear (i.e. to leave kinks in the case of self-diffusion or to be deposited in the case of heterodiffusion) and to gain some energy (sufficient for hopping). It is suggested that during thermally activated tracer diffusion adatom does not interact with any other diffusion objects.

As it was already noted for system with constant energy ‘to reach thermodynamic equilibrium’ means to reach the maximum of entropy. That is a reason why non-interacted atoms diffuse to side of clean Si surface for increasing of entropy S (U does not change). This process could be depicted by second Fick equation:

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

It must be emphasized that exactly speaking, this equation holds for cases where \(D\) is unaffected by the concentration.

**The case of interacted particles.** Another situation takes place on the surface when the interaction energy of adsorbate atoms is high (high density of adsorbate) and the internal energy \(U\) of system is variable. Then, on the one hand, diffusion process must be directed to equalization of the foreign atoms concentration on the surface (i.e. atoms have to move along the surface to increase the entropy). On the other hand (when surface adatoms concentration is enough and they start to interact) surface phase silicon-adsorbate has to form (i.e. ‘diffusing’ atoms have to stop). Let us examine this paradox and the link between the surface diffusion and phase transitions.
a) The initial view. Carpet diffusion. It was first suggested by Gomer [21] to explain diffusion of gas multilayers on metals. Gomer explained that the first monolayer of gas atoms is chemisorbed and immobile while atoms of the next monolayer are physisorbed and mobile. The same behavior was found for a lot of metal-on-metal systems where the first monolayer is strongly adsorbed and, practically, immobile.

In that event surface tends 'to be covered' by adsorbate atoms (like by carpet) and next absorbate atoms (atoms in excess to 'first layer of adsorbate') move along this carpet to occupy clean substrate surface, as it was shown on Fig. 8a. This mechanism named 'mechanism of an unrolling carpet'. To cite one more analogy of this type diffusion, let us imagine a hill of sand on the surface covered by glue (Gegusin et al. [19]). Wind blowing parallel to the surface causes the sand grains motion. But the grains of sand, which are brought on the surface covered by glue, will stop their motion in spite of wind. The grains' migration proceeds only on the surface covered by sand. Hence, the migration of substance A along the surface of substance B appears as a migration of substance A on the monolayer of substance A covering B [19].

One should note that mechanism of surface diffusion of interacted atoms actually is more complex.

In the case of interacted atoms, $D$ is a function of concentration $c$ and second Fick equation can be written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

(6)

The solution of this equation is strongly dependent on boundary and initial conditions. However, equation (5) can yield good results to govern the diffusion process in the case of small concentration of diffusant or small gradient of concentration. Such situations are of frequent occurrence in experiments.

b) Surface phases formation and surface heterodiffusion. In the early 1980s the role of surface phases' formation during metal atoms diffusion on semiconductor (Si) substrate (using AES, LEED and electron microscopy techniques) has been investigated in ref. [22].

In the experiment, diffusion of Au atoms out of a gold strip about 10 ML thick and 1 mm wide was carried out in the temperature range 500-900°C. At the initial period of annealing, the continuous Au film disintegrates into separate 3D islands covering about 5% of the area. The surface area within the strip between islands is occupied by Si(111) $\sqrt{3} \times \sqrt{3}$-Au surface phase. The Au diffusion proceeds via the release of Au atoms from the islands and the motion of thus formed adatoms over the surface phase out of the strip. Diffusion is significantly retarded after depletion of 3D islands.

The spreading of Au overlayer was found to be accompanied by Si-Au surface phases’ formation. One can see in Fig. 13 that Au concentration profile consists of regions with different slopes corresponding to regions of different surface phases on Si substrate. This implies that the diffusivity of 'on phase' atoms varies from one phase to another. Only a gradient of these atoms defines the character of diffusion ('in phase' atoms are relatively immobile).

Experimentally determined diffusion constants for different phases in Au/Si(111) system are presented in Table 1. The difference in activation energy of migration for 'on phase' atoms on various Si-Au surface phases makes it possible to control the concentration profile by adjusting the annealing temperature. One can see in Fig. 13a that at 660°C diffusion proceeds through the propagation of Si(111) $\sqrt{3} \times \sqrt{3}$-Au surface phase only. This is due to the fact that at this temperature the coefficient of diffusion of Au adatoms is higher for $\sqrt{3} \times \sqrt{3}$ surface phase than for $5 \times 2$ one.

c) Si(111) $\sqrt{3} \times \sqrt{3}$-Au. In this division we discuss the results of extra-thin gold strip (about 1 ML) annealing. At relatively low temperatures (600°C) there is no diffusion during annealing, since all gold atoms incorporate to Si(111) $\sqrt{3} \times \sqrt{3}$-Au surface phase and there are no 'on phase' atoms for diffusion. The increasing of temperatures leads to the surface phase Si(111) $\sqrt{12} \times \sqrt{12}$-Au disruption with the resulting formation of the 'on phase' atoms formation, their diffusion and Si(111)5 2-Au surface phase formation (Fig. 14).

d) Si(111)-In. The similar results was obtained during investigation of Si(111)-In system. Fig. 15 clearly shows plateaus corresponding to In 'on phase' atoms diffusion on the different Si-In surface phases.

e) Present view. Diffusion as a variant of interface formation. Here we compare 'carpet diffusion' mechanism with present concept. Particular attention has been given to the discussion about the role of surface phases formation in surface diffusion.

(i) Classic 'carpet diffusion' model (in which it was supposed, that initially surface covers by one monolayer of adsorbate) ignored the tendency of surface to reach minimum of free energy, i.e. to form surface phases consisting of adsorbate and substrate atoms (according to adsorbate-substrate phase diagrams). The concentration of foreign as well as substrate atoms’ constituent of surface phase can be essentially differs from one monolayer. Thus, during diffusion process the surface can be covered by various amounts of relatively stable foreign atoms (and substrate atoms as well), which are practically immobile.

(ii) To form surface phase (immobile layer) respective concentration of foreign atoms, substrate atoms and temperature are necessary. The way of delivering of foreign (and substrate) atoms may be different: deposition, accumulation of dopant atoms during evaporation of substrate atoms (Si(111)$\sqrt{3} \times \sqrt{3}$-B formation by annealing of highly B doped Si [13]), etc. Surface heterodiffusion is also a ‘method’ of delivering of foreign atoms (substrate atoms are usually sufficient to form a surface phase at 'equilibrium' temperatures used).

### Table I: Diffusion constants for different Si(111)-Au surface phases.

| Surface phase | $D_0$ (m$^2$ s$^{-1}$) | $E$ (eV) |
|---------------|-----------------------|---------|
| Si(111) $\sqrt{3} \times \sqrt{3}$-Au | $0.7 \times 10^{-4}$ | 1.3 |
| Si(111) $5 \times 2$-Au | $4.75 \times 10^{-3}$ | 1.6 |
| Si(111) $7 \times 7$ | 0.12 | 2.0 |
FIG. 13: Concentration profile obtained for Au surface diffusion on Si(111) at (a) 660°C, (b) 900°C. Regions of different surface phases: (II) $\sqrt{3} \times \sqrt{3}$; (III) $\sqrt{3} \times \sqrt{3} + 5 \times 2$; (IV) $5 \times 2$; (V) $5 \times 2 + 7 \times 7$; (VI) $7 \times 7$. Dashed line shows the Au strip edge. From Ref. [22].

(iii) Any accumulation of interacted foreign atoms on the substrate’s surface phase during their deposition (of course, we deal with submonolayers) leads to new surface phase formation. Next accumulation of an ‘on phase’ atoms on the last surface phase leads to the production of following surface phase and etc, see Fig. 13. Thus, stages of interface formation are a changing of surface phases one after the other and accumulation ‘on phase’ atoms in between. The same situation as a result of accumulation of foreign atoms one can see during surface heterodiffusion.

(iv) During surface diffusion surface phase starts to form initially from a small surface area where concentration of foreign atoms reaches a value, when foreign atoms begin to interact with each other. Before this, diffusion process may be depict by the equation (6) for non-interacted atoms, which diffuse on different surface phases, see areas VI, IV and II in Fig. 13.

(v) When all surface is covered by surface phase next small amount of diffusing foreign atoms act as ‘on phase’ atoms which weakly bonded with substrate, does not interact with each other and have a high diffusion mobility. When their concentration reach the critical value in order to form next surface phase, ‘on phase’ atoms spends for 2-D islands of surface phase formation and act as immobile ‘in phase’ atoms. It reduce the driving force of diffusion connected with the concentration gradient of diffusing ‘on phase’ atoms and slow down diffusion flux in comparison with the case of ‘on phase’ (non-interacting atoms).

f) Conclusions. As was described, process of ‘interacted particles diffusion’ can be explain by competition of two ‘driving forces’ which reduce system’ free energy $F$: increase of entropy $S$ at the cost of equalization of the foreign atoms concentration along surface and reduction of internal energy $U$ due surface phase formation. When particles do not interact (concentration is small) first process occurs. When particles start to interact (that is their concentration is sufficient) diffusion process stopped and system gains some free energy as result of surface phase formation (a gain in $\Delta U$ is high). In the last case ‘observed’ diffusion occurs as result of ‘on phase’ atoms (adatoms) on formed regions of new surface phases.

Generally, the problems of chemical diffusion are still not completely understood and gap between theory and experiment persists today (see, for example, review [18]).

C. Surface self-diffusion (mass transport)

It is necessary two events occur in order that adatoms are involved in process of the surface self-diffusion: 1) formation of adatom (atom must leave a kink of step); 2) adatom has to gain some energy for hopping. On the second stage the role of surface phase formation could be essential.

Very often the process of the Si surface self-diffusion is convenient for analysis in the non-equilibrium systems (case a goal-directed surface diffusion) by nondirected methods (for example, light surface scattering). Let us discussed the common ideas of a goal-directed surface diffusion and the method of the light surface scattering.

A goal-directed surface diffusion. Goal-directed surface self-diffusion is much in evidence on migration of own atoms of crystal on the surface with some defects like scratches. The ‘aim’ of a goal-directed surface self-diffusion in this case must be the tendency for a decrease the surface free energy as a result of repairing the scratched surface to scratch-free one (see Fig. 16). The main feature of this process is the availability of substantial diffusion flux in certain direction (to cover scratch by atoms to decrease surface area). It means that the number of atoms moving to scratch is higher than that of ones moving from scratch. Diffusing atoms take part in two motions: disordered diffusion on the surface and directed diffusion to scratches.

Steps are a source of atoms, which fill scratches. Atoms
leaving the knocks of steps can move to the scratch. It is obvious that as this takes place the steps have to move in the opposite direction (Fig. 16). It means that steps’ motion is necessary for goal-directed self-diffusion. When it is impossible for some reason (for example, there is some mixture of foreign atoms along the steps and such steps cannot move) directed self-diffusion does not occur.

**Indirect methods of the self-diffusion analysis and problems.** For the investigation of self-diffusion in ultrahigh vacuum conditions the surface migration is studying indirectly, usually, by modeling of some process (growth, phase transitions, smoothing and so on). This results in the spread of values for diffusion constants. In these cases attention has to be given to reasons for surface mass transport. It should be emphasized that if the different ‘driving forces’ of surface transformations are available, a variation in diffusion parameter will result.

A direct observation of the atomic migration (for example, by scanning tunneling microscopy (STM)) looks much more preferable. However, STM method, which is very convenient for chaotic diffusion analysis of individual atoms at small diffusion distances, receives a lot of difficulties to use for investigations of collective mass transport at large distance.

**Mass transfer diffusion and light scattering method.** Experiments related to the self-diffusion constants’ determination often consist in the in situ analyzing of surface roughness spectra transformations using laser or electron beam. Mass transport due to gradient of cur-
vature on Si surface has been studied in [23]. To provide the information concerning surface self-diffusion the method of light scattering has been used. The heart of this method is the intensity measurements of light scattered by superposition of sinusoidal harmonic (totality of them forms the surface roughness) during their smoothing. Every harmonic with period $\lambda$ reflects light in the certain direction (at an angle $\varphi$ corresponding to this $\lambda$). Light intensity $I(\lambda, t)$ at the certain angle $\varphi$ decreases exponentially during annealing:

$$I(\lambda, t) = I(\lambda, 0) \exp\{-2\kappa(\lambda)t\},$$

where $\kappa(\lambda)$ is function of surface diffusion, $t$-time of annealing, see Fig. 17. Measurements of $I(\lambda, t)/I(\lambda, 0)$ ratio enable $\kappa(\lambda)$ (and, as a result, surface diffusion coefficient) to be found for different temperatures of annealing. In turn, this makes it possible to calculate diffusion constants.

The activation energy of Si surface self-diffusion (mass transfer) determined in [23] is 2.2 eV. This value is in a very good agreement with data of others group received by scratch decay method [24] and obtained by STM and LEED [25]. The activation energy inferred from such experiments is essentially higher than for tracer diffusion measurements. This is no surprise, since activation energy of adatom formation into the measured values of activation energy of self-diffusion is included [23]. This part of activation energy strongly depends on experimental conditions (roughness, shape of steps etc.). Two-component Si-Me surface phase formation on Si surface leads to increasing of diffusion rate of Si self-diffusion process [26].

### D. Anisotropy of surface diffusion and surface phases

It is well known, that surface diffusion process is anisotropic even on 'ideal' crystal surface since crystalline properties are dissimilar in different directions. Diffusion coefficient depends on activation energy $\Delta E$ and preexponential factor $D_0$, which, in turn, is related to the height of diffusion barrier, the mean-square jump length, and the mean vibrational atomic frequency in quasi-equilibrium position. All these quantities depend on crystallographic directions. The similar situation holds, when we analyze diffusion of adatoms on anisotropic surface phase. The typical example of directional surface diffusion on the surface phase is shown in Fig. 18. On this figure one can see anisotropy effect of Ag diffusion on Si(111)4×1-In surface phase. Silver atoms diffuse along In rows essentially more rapid than in normal direction. As a result the forming Ag islands are of oblong shape.

### E. Surface diffusion, surface phases and outer driving forces. Surface electromigration

Electromigration (in the bulk or on the surface) is a preferential mass transfer towards either the cathode or the anode due to electrical current or electrical field applied to the sample. It is known today that the driving force of the electromigration consists of two components: the electrostatic force and the carrier (for example, electron) wind force, see [27]. The former is a result of influence of electric field on the ionic charge of atoms, which can move along the sample. The term 'carrier wind' or 'electron wind' needs to be explained. Usually, a wind generated by the pressure difference of the air can transfer loosely held objects. We can say the same about 'electron wind' which is caused by momentum transfer to an atom from electrons during electron motion in the electric field. The driving force $F$ acting on a single atom is

$$F = Z^*qE,$$
where $Z^*$ is the effective charge number, $q$ the elementary charge, and $E$ the electric field. $Z^*$ is divided into an electrostatic part $Z_{el}$ and a wind part $Z_w$ as

$$Z^* = Z_{el} + Z_w. \quad (9)$$

If the current carriers are electrons, the electron wind force is directed to the opposite side to the electrostatic force. It is well known, that bulk electromigration of metals in semiconductors is directed towards the anode. In the bulk a wind part $Z_w$ is more essential.

Surface electromigration has been studied first by Zhou et al. [27] and Yasunaga et al. [28]. It was found that $Z^*$ is -8 to -30 for electromigration of metals on silicon substrate and that surface electromigration can occur in both directions (to the anode or to the cathode).

One can see that the diffusion without electromigration (see Fig. 15) is accompanied by Si(111)$\sqrt{7}\times\sqrt{3}$-In and Si(111)$4 \times 1$-In surface phases formation, see Section 2.2. Si-In surface phase formation at the diffusion with electromigration is also detected by Yasunaga et al. [28]. These experimental results show a preferential surface mass transport with external driving force to DC current direction. The spread of different surface phases (Si(111)$\sqrt{7}\times\sqrt{3}$-In and Si(111) $4 \times 1$-In) is also (like without 'electromigration') occurs due to the conditions of these surface phases' formation (i.e. due to Si-In surface phase diagram) and to distinct diffusion activation energy of In 'on phase' atoms on $\sqrt{7}\times\sqrt{3}$ and $4 \times 1$ phases. The distinctions between diffusion processes 'with' and 'without' electromigration lies only in kinetics of delivering of sufficient number of In atoms for surface phases formation.

III. ADSORPTION (DESORPTION) AND SURFACE PHASES FORMATION

A. Adsorption and interface formation

Adsorption and interface formation at equilibrium situation occurs by the same way as diffusion process, namely: accumulation of 'on phase' atom at Si surface, surface phase formation, accumulation of 'on phase' atoms at first surface phase, reordering to the next surface phase with more density of foreign atoms and so on. Surface diffusion is example of initial stages of interface formation since important things are quantity of foreign atoms at the surface and temperature of substrate but way of delivering of these atoms is not essential. Very important is such characteristic of interface phenomena as deposition rate. It characterized equilibrium or nonequilibrium process occurs which is essential for epitaxial growth of metallic and silicide films on Si. The deposition rate has to be not higher than it is necessary for ordered surface phase formation, which can be used as template for epitaxial films growth.

B. Desorption and surface phases

In this section we discuss the role of surface phases formation during desorption process. In work [22] the direct monitoring of the In surface concentration during desorption by AES was accompanied by LEED observations. In this experiment, an In film about 10 monolayers thick on Si(111) was annealed isothermally at a temperature in the 400-550°C range. As a result of annealing the surface was covered by Si(111)$\sqrt{7}\times\sqrt{3}$-In and islands which occupied about only 5% of the area. One can see from Fig. 19 that during the first 6 min the In coverage remains constant ($\theta_{in} \sim 1.5$ ML). This value approximately corresponds to the In concentration in the Si(111) $\sqrt{7}\times\sqrt{3}$-In surface phase. Desorption from this surface phase is compensated by In diffusion from the islands. After the disappearance of the islands the In concentration begins to decrease but LEED pattern remains $\sqrt{7}\times\sqrt{3}$. It is 'the region of homogeneity' of this surface phase. When the In concentration reaches the critical value a sharp reordering into a 'less density' phase takes place. This reordering is accompanied by a step-like decrease of the In concentration due to desorption of adatoms which do not belong to the new phase. The coverage of In atoms in the next surface phase $4 \times 1$ is 0.75 ML. The atoms that are in excess to this concentration desorbed from the surface since the binding energy of these atoms is very small. Then desorption again proceeds according to the exponential law:

$$C(t) = C_o \exp(-t/\tau), \quad (10)$$

where $C(t)$ is the concentration at moment $t$, $C_o$ is the initial In concentration and $\tau$ is the life time of an In atom in the surface phase. From the temperature dependence of

$$\tau(T) = \tau_0 \exp(E/kT), \quad (11)$$

the desorption parameters for the observed surface phases were determined (see Table 2). The constants of desorption are different for the various surface phase. These results show that the desorption kinetics is determined by the sequential replacement of surface phases characterized by the different binding energy of the atoms within the surface phase and of adatoms with the surface phase.
Three components surface phase’s formation.

Let us consider different cases of two- and three-component surface phases. Thus the term adsorbates concentration, substrate temperature and surface conditions. Hence the term coadsorption’ will be thereafter generally adopted for any situations in which two kinds of adsorbate atoms will appear on the surface. Let us consider different cases of two- and three components surface phase’s formation.

A. Two-components surface phases formation

1. Si-A(B) surface phases formation on Si(111)

Si-Ag-H, Si-Al-H. The problem of structural transformations on Si surface covered by H and metallic atoms is under investigations more than 10 years. Fig. 20 could illustrate some common results [29]. For these kinds of adsorbates on Si(111) surface two-component Si-H surface phase formation is preferable. Thus, both systems (Si(111)-Ag-H and Si(111)-Al-H) demonstrated the similar behavior: 1) H atoms displace metallic atoms and form Si(111)-H surface phase; 2) metallic atoms agglomerates to the islands; 3) H desorption leads to recovering Si-Ag (or Al) substrate phase. The distinction between these two cases are in the temperature of recovering Si(111)\(\sqrt{3}\times\sqrt{3}\)Ag and Si(111)\(\sqrt{3}\times\sqrt{3}\)Al.

Si-Ag-In. Coadsorption of two kinds of metals occurs by the same manner. After deposition of In atoms onto Si(111)\(\sqrt{3}\times\sqrt{3}\)Ag and annealing at 400°C Si(111)-Ag surface phase starts to destroy and ordered Si(111)-In surface phases start to form. As a previous case Ag atoms agglomerate to the islands.

TABLE II: Desorption parameters of In from the Si-In surface phases.

| Surface phase | \(\tau_0\) (s) | E (eV) |
|---------------|----------------|--------|
| Si(111) \(\sqrt{7} \times \sqrt{3}\)-In | \(2.5 \times 10^{-3}\) | 0.9±0.2 |
| Si(111) 4\times1-In | \(5.7 \times 10^{-8}\) | 1.5±0.2 |
| Si(111) \(\sqrt{31} \times \sqrt{3}\)-In | \(3.6 \times 10^{-11}\) | 2.0±0.3 |

IV. COADSORPTION

All processes on surface are determined by the interaction between adsorbate-adsorbate, adsorbate-substrate and substrate-substrate atoms. If we add the second adsorbate, the situation becomes more complicated and simultaneously more interesting. In the case of codeposition of two kinds of foreign atoms some atoms act as ‘on phase’ atoms and other one as ‘in phase’ atoms.

If the bonding energy of Si-A surface phase (A is the kind of foreign atoms) is larger than that of Si-B one and free energy of Si-A surface phase is less that of Si-A(B) three-component surface phases (or these three-component surface phases do not exist) - in this situation Si-A surface phase can be formed at equilibrium conditions at Si-surface. In the cases free energy Si-(A,B) surface phases are less - three-component surface phases with new superlattice (or solid solution type) will be formed.

Of cause, in the both cases the final situation is unaffected by the order of adsorbrates deposition (simultaneously or sequentially) at the equilibrium conditions and is defined by the adsorbates concentration, substrate temperature and surface conditions. Thus the term coadsorption’ will be thereafter generally adopted for any situations in which two kinds of adsorbate atoms will appear on the surface. Let us consider different cases of two- and three components surface phase’s formation.

2. (A-B) surface phases formation on Si(111) (Al-N, B-N and InSb on Si(111))

Next three examples are related to cases of two-components surface phases formation from adsorbate atoms. Deposition of Al atoms on Si(111)-N surface phase or ‘deposition’ of N atoms on Si(111)-B surface phase leads to the similar results - adsorbate-adsorbate surface phases construction. Fig. 21 shows the surface transformations after Al deposition [30]. Auger date (Fig. 21f) clearly demonstrate that annealing of 1 ML Al films deposited on Si(111)-8 \times 8-N leads to breaking Si-N bonds (Auger peak 83eV which is corresponding to Si-N bonds disappeared), Al-N bonds formation (Auger peak of clean Al 69 eV is shifted to another position 59 eV), and ‘clean’ Si restoring (Auger peak of Si looks like peak of clean Si(111) on Fig. 21a).
BN surface phase were formed on Si(111) substrate by exposure in air Si(111)$\sqrt{3}$×$\sqrt{3}$-B surface phase. Annealing of this system at 900°C gave rise to the breaking of Si-B bonds and to the B-N bonds occurring [31]. Auger date shows 'chemical shift' of the peak 180 eV corresponding to B from the Si(111)$\sqrt{3}$×$\sqrt{3}$-B surface phase to the new position 173 eV, which is corresponding to the B in BN surface phase.

Another attempt to create an (A-B) surface phase on the Si(111) using coadsorption of group-III and group-V elements was performed in Refs. [32,33]. This structure is found to be formed after 1 ML Sb adsorption onto the pre-formed Si(111)$4 \times 1$-In phase above about 250°C. Adsorbed Sb atoms ruin the initial In structure incorporating between In and topmost Si layers forming an 2 × 2-InSb surface phase on top of bulk-like Si. At that Sb layer has a (1 × 1) lattice and In atoms are arranged in the honeycomb-like network on top of Sb layer having a (2 × 2) periodicity. It is necessary to emphasize that the structural arrangement of this phase is similar to that of the surface phase of clean InSb(111) substrate, namely InSb(111)-A(2 × 2) [33] as was confirmed by STM experiments (Fig. 22). However, the difference in lattice constants between the InSb(111) and Si(111) substrates (over 19%) leads to strain accumulation and results in significant number of defects. This structure exists only under the deficit of Sb atoms (below 1 ML). When Sb coverage reaches 1 ML that is saturation coverage for the 2D In gas condensation. This explains the absence of the gold Auger peak. Isothermal desorption experiments of 2D In gas condensation. This explains the absence of the gold Auger peak. AES analysis showed that the In film thickness changes by desorption [34]. Fig. 23a and Fig. 23b demonstrated that as a result of In deposition onto Si(111)$5 \times 2$-Au or Si(111)$\sqrt{3}$×$\sqrt{3}$-Au followed by annealing at 300-500°C causes disappearance of the gold Auger peak. AES analysis showed that the In film thickness corresponds to the composition of the Si(111) $\sqrt{7}$×$\sqrt{7}$-In surface phase.

It is well known that diffusion of gold into a silicon substrate does not occur at 300-500°C. On the other hand, gold desorption from the Si surface becomes noticeable only at temperatures exceeding 850°C [35]. The above facts may be interpreted as follows. Agglomeration of gold atoms into the islands covered by indium atoms takes place on the Si surfaces upon annealing of deposited Au and In films. The gold islands serve as additional centers of gold desorption. Isothermal desorption experiments with such a three-component system confirm the presence of gold on the silicon surface. As In evaporates, the Au Auger-peak appear; its amplitude increases rapidly up to the initial level corresponding to the Si(111)$5 \times 2$-Au surface phases. A new three-component surface structure formation.

B. Codeposition and three-components surface phases formation

In this division examples of the different kinds of Si-Au-In three-components surface phases formation will be discussed.

Si-Au-In. It is difficult to know the certain concentrations of metals that are necessary to Si-Au-In three-components surface phases formation. It was a reason to organize the experimental procedure in which In coverage was changing by desorption [34]. Fig. 23a and Fig. 23b demonstrated that as a result of In deposition onto Si(111)$5 \times 2$-Au or Si(111)$\sqrt{3}$×$\sqrt{3}$-Au followed by annealing at 300-500°C causes disappearance of the gold Auger peak. AES analysis showed that the In film thickness corresponds to the composition of the Si(111) $\sqrt{7}$×$\sqrt{7}$-In surface phase.

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Si(111)-In surface phase with 1 mm wide deposited with Au strip: (a) before annealing, (b) after annealing (300$^\circ$C, 1 min), (c) isothermal desorption of In at temperature 500$^\circ$C, I Si(111)$\sqrt{7}$×$\sqrt{3}$-In, II Si(111)3×1-(Au,In), III Si(111)4×1+5×2-(Au, In), IV Si(111)5×2-Au. From Ref. [34].

Si(111)3×1-(Au,In) is formed at intermediate coverage of In and Au, see Fig. 23c.

Si-Ag-Au. The new type of three-component surface phases formation (solid solution) is shown on Fig. 24. It was founded [34,36] that at the small Au coverage (less than 1/3 ML) gold atoms are incorporated in Si(111)$\sqrt{3}$×$\sqrt{3}$-Ag surface phase lattice. The increasing of the Au coverage leads to Si(111)$\sqrt{3}$×$\sqrt{3}$-Au surface phase formation with the replacement of Si-Ag by Si-Au surface phase.

V. ROLE IN SURFACE CONDUCTIVITY

Due to the difference between electronic structures of bulk and surface phases one can expect that electrical properties of them are quite different [37,38,39,40,41]. The conductance in a 'surface phase layer' will differ from the conductance of a bulk layer of the same dimensions [42]. Therefore when we deal with surface phase on silicon substrate one should explain surface transport in the frame of model 'two substances which are in contact (bulk phase and surface phase). The electrical conductivity of surface phase very often is quite essential enough and its easily can be obtained by usual four-point probe method carrying out in situ.

A. Electrical conductance after deposition at room temperature

The thickness of surface phase is conventionally very small (order of magnitude is several Angstroms). In this case it is obvious that the probes contact with SP itself and with the bulk substrate. Consequently, the current passing through the sample with surface phase Si(100)2×1 is divided on two components: the surface substrate and through the surface phase. If propose that surface phase has its own properties that are different from the bulk one including conductance the destruction of this SP undoubtedly leads to the disappearing of this two-dimensional conducting channel on the surface, and component $\sigma_2$ (Fig. 25a) is break. That is measured conductivity is to decrease due to the destruction of the conductive channel, i.e. $\sigma = \sigma_1$. Firstly, such result was obtained by Henzler et al. [37]. They investigated surface conductivity of clean Si(111) surface and discovered the decreasing of conductivity as a result of disruption of Si(111)2×1 surface phase [37], see Fig. 26. The similar behavior was obtained for two-component surface phase. Fig. 27 shows the conductivity changes in the Au/Si(100) submonolayer system after Au deposition at RT [41]. The regions of surface structures' existence observed by LEED are indicated on this figure. At initial stage of Au adsorption abrupt decreasing of reflection intensity and background intensification in LEED pattern is registered. At following deposition LEED images show diffuse 2×1 pattern. After 0.6 ML of Au deposition 1×1 pattern is observed. As 2×1 superspots are weakened therefore the ordered structure of Si(100)2×1 surface phase is broken and conducting channel formed disappears. Hence the conductivity decreases at initial stage of Au adsorption and begins to increase only at adsorbate coverage of about 0.5 ML due to formation of metal film.

B. Electrical conduction of surface phases silicon-adsorbate

Let's consider, for example, the Si(100) substrate. The formation of surface phases silicon-adsorbate results in appearing of new conducting channels on the surface. Due to the shunting effect of the bulk substrate the contribution of the surface phases in conductivity of the bulk substrate is measured. In this case the changes of conductivity have to indicate the increasing of conductivity if the conductance of surface phase Si(100)-adsorbate is greater then that for Si(100)2×1 surface phase and decreasing of conductivity if conductance of surface phase silicon-adsorbate is less than one for Si(100)2×1 (Fig. 25b).

Si(100)-Au. After Au adsorption at RT and annealing at 850$^\circ$C on Si(100) surface at Au coverage about 0.5 ML
c(8 × 2) superstructure is observed corresponding the formation of Si(100)c(8 × 2)-Au surface phase. At coverage of about 1 ML Si(100)√26 × 3-Au surface phase forms. The surface conductivity increases for observed surface phases correlating with formation of new conductive channels on the surface: difference in surface conductivity Δσ is $(6.0 \pm 1.9) \times 10^{-5} \ \Omega^{-1} \text{Square}$ for Si(100)c(8 × 2)-Au surface phase and $(11.1 \pm 0.8) \times 10^{-5} \ \Omega^{-1} \text{Square}$ for Si(100)√26 × 3-Au surface phase. It is seen that the difference in conductivity is connected with adsorbate coverage in surface phase silicon-adsorbate. It was observed that surface conductivity increasing of the Si(100)-Au system is proportional to the Au coverage of the Au/Si(100) surface phase and thus the conductivity is proportional maximum concentration of charge carriers which is possible for this system. The atom density in Si(100)√26 × 3-Au surface phase is higher by a factor of two than that for Si(100)c(8 × 2)-Au (Au = 0.5 ML for c(8 × 2) and Au = 1 ML for √26 × 3 superstructure [43]) and, hence, we see the twice increasing of surface phase contribution to the surface conductivity. Thus, it seems likely that a main role of surface phase channels in conductivity is formation of its own number of charge carriers. The area of transport is near surface region.

FIG. 24: The behavior of the films with different ratio of Au and Ag atoms on the Si(111)7 × 7 surface co-deposited at room temperature followed by annealing at 450°C. 1 - surface atomic concentration before annealing; 2 after annealing; 3 concentration no changed after annealing.

The role of surface roughness. It was shown that the difference in surface conductivity of Si(100)2 × 3-Na SP $\Delta \sigma = -(1.5 \pm 0.6) \times 10^{-5} \ \Omega^{-1} \text{Square}$ has an opposite sign in comparison with the Si(100)-Au SP [41]. Note, that the formation of the 2 × 3-Na SP by Na deposition on Si(100) surface and annealing (Na coverage is about 1/3 ML [44]) reduces the surface conductivity. In this case the structural transformations of the surface during the formation of Si(100)2 × 3-Na surface phase play dominant role in reduction of conductivity. It is known that formation of this surface phase involves a substantial redistribution in the top Si(100) substrate layer (i.e. surface Si mass transport). Silicon surface with flat terraces converts to the surface which contains numerous small domains dividing by monoatomic steps [5]. As was shown in [14] the reduction of conductivity of sample with Si(100)2 × 3-Na can be associated with the change of the surface roughness and size changes of the 2 × 3-Na domains. The exposure of the sample with Si(100)2 × 3-Na surface phase in atomic hydrogen results in decreasing of conductivity [45] which is connected with destruction of this surface phase as in the case with Si(100)2 × 3 surface. It indicates that Si(100)2 × 3-Na surface phase forms the additional conducting channel despite the conductiv-
FIG. 25: Schematic illustration of surface phases as conductive channels on the surface: a) destruction of surface phase Si(100)2×1 at RT and disappearing of conductive channel, b) formation of new conductive channel formed by surface phase silicon-adsorbate. σ1 - conductance of silicon substrate, σ2 - conductance of Si(100)2×1 surface phase, σ3 - conductance of Si(100)-A surface phase.

FIG. 26: Changes in surface conductivity and LEED pattern after isochronal annealing. The measurements were done at RT. From Ref. [37].

FIG. 27: The surface conductivity and LEED changes of Au/Si(100) submonolayer system at Au deposition at RT onto Si(100)2×1 surface phase. The measurements were done at RT.

VI. CONCLUSIONS

In this review we would like to demonstrate the role of surface phase formation in the various surface processes like surface diffusion, adsorption, desorption and so on as well as in surface conductivity. It was emphasize that Si surface phases are new kind of two-dimensional substance, which are formed on Si surface at the equilibrium conditions at the surface. Thus, all processes at the Si surface are directed to the surface phases formation and it is not possible to understand any surface processes without understanding of this. Si surface play the main role as arena of surface processes but some times also acts as Si atoms source.

It is not to say that on the Si surface only two-dimensional phases can be formed. The last investigations show that a specific regions of Si surface act as one or zero-dimensional arena. It leads to quantum wires and quantum dots formations in such areas subjects of nanoelectronics. But we believe that the formation of these nanomaterials will occurs according to the similar principles and laws and this paper will be helpful for investigators of all low-dimensional structures.

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