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A scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS) was held on 23 February 2000 at the P L Kapitza Institute for Physical Problems, RAS. The following reports were presented.

(1) **Lifshits V G, Gavrilyuk Yu L, Saranin A A, Zotov A V, Tsukanov D A** (Institute of Automation and Control Processes, Far East Division of the Russian Academy of Sciences, Vladivostok) "Surface phases on silicon";

(2) **Andryushechkin B V, El'tsov K N, Shevlyuga V M** (Center of Natural Science Research, Institute of General Physics, Russian Academy of Sciences, Moscow) "Scanning tunneling microscopy of 'commensurate – incommensurate' structural phase transitions in the chemisorbed layers of halogens";

(3) **Molotkov S N** (Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow region) "Spin effects in tunneling microscopy";

(4) **Maslova N S, Panov V I, Savinov S V** (Lomonosov Moscow State University, Physics Department, Moscow) "Tunneling spectroscopy of the localized states of individual impurity atoms on a semiconductor surface".

Summaries of three papers are given below.

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Surface phases on silicon

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This paper gives an idea of what should be taken as the composition of surface phases on silicon, provides examples of how the number of silicon atoms involved in the formation of these phases should be determined, and describes experimental data on surface-phase conductivity.

Surface phases. If a system of interest consists of two contacting homogeneous bulk parts in different states which are in equilibrium with each other, these parts are said to be the phases of a substance [1]. On the surface, as in the volume of a solid, all processes progress toward the establishment of a thermodynamic equilibrium in which there is no directional atom transfer, that is, toward the formation of phases, in this case surface phases, that are in equilibrium with a volume phase. Thus, it can be said that a surface phase (SP) is a surface layer existing in thermodynamic equilibrium with a volume and possessing its own electron and crystal structure and properties [2].

Structure and composition of surface phases. Among other properties, a geometrical structure is considered to be one of the most important features of surface phases, allowing them to be identified with much success. It is common practice to designate SPs according to their periodicity relative to a single-crystal substrate on which they are grown. For example, in the case of an Si(100) 2×3-Na SP, the lattice constants along the x and y axes are, respectively, two and three times greater than those for a (100) silicon substrate.

When considering the formation of an SP, a distinction needs to be drawn between atoms entering into the composition of the SP ('in-phase' atoms) and atoms present in excess relative to the concentration of foreign atoms when the surface is entirely covered by the SP ('on-phase' atoms). To specify phase composition, the term 'adsorbate coverage' is usually used. Let us clarify this term by an example. Let us assume that the outermost surface layer of Si(100) contains 6.8×10^{14} atom cm^{-2}. If just as many foreign atoms as there are Si atoms are evaporated onto the surface, we deal with a 'coverage' (θ) equal to one monolayer (ML).

Role of silicon atoms in the formation of surface phases. The fact that the surface of silicon is 'reconstructed' after evaporating adsorbate onto it and bringing the system to equilibrium (that is, Si atoms escape from positions occupied by them in the volume lattice) was known long ago. It was believed that silicon atoms in the surface monolayer rearrange themselves and make chemical bonds with adsorbate atoms. This manifests itself, for example, as chemical shifts in the Auger spectra of Si [3]. In addition, it was assumed that only the number of adsorbate atoms entering into an SP is essential for determining its composition, whereas the amount of silicon entering into the composition of any SP is always equal to one monolayer. Therefore, the term 'coverage,' designating the total number of foreign atoms deposited onto a surface, was rather convenient to use.

However, it does not always happen that only 1 ML of silicon atoms underlies the adsorbate layer. When submonolayer metal coatings are applied to a silicon substrate at elevated temperatures, any ordered silicon SP disintegrates, which results in the formation of unbound metal atoms and 'unoccupied' silicon atoms. These atoms may combine with each other in the *appropriate proportions* to form an SP with a new type of crystal lattice differing from the silicon lattice and overlaying the latter epitaxially (that is, in the form of a two-dimensional single crystal). To describe such an SP, *not only the content of adsorbate atoms, but also the content of silicon atoms should be indicated* (just as is done for two-component volume phases — A_xB_y), *and the amount of silicon does not*

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need to be equal to one monolayer. The problem is in determining the 'in-phase' silicon atoms, since it is not easy to distinguish silicon atoms entering into the composition of an SP from those entering into the composition of the substrate. The problem has been solved using scanning tunneling microscopy (STM) [4, 5]. It was suggested that the formation of a two-dimensional island of a two-component SP with the amount of silicon differing from that in the surface layer of the substrate must be accompanied by mass transfer over the surface of the substrate with the formation of a pit. Such a process is illustrated in the figure.

Designating the area coated by the islands of the Si(100)2×3-Na SP as s and the density of silicon atoms in this phase as θ_s, one can write the equality of the flows of silicon atoms leaving the substrate and atoms incoming to form an Si(100)2×3-Na SP:

$$(1-s)(1-\theta_s) = s\,\theta_s\,.$$

From this equation, having a knowledge of the area coated by the Si(100)2×3-Na SP islands, one can determine θ_s (in this case $\theta_s = 1/3$ ML). Note that, according to Ref. [6], θ_s for Na is also equal to 1/3 ML.

A knowledge of the amounts of metal and silicon atoms involved in the formation of the Si(100)2×3-Na SP allows one to write its composition formula as SiNa. For example, the Si(100)4×3-In SP has a different formula, namely, $Si_{0.5}In_{0.6}$ [7]. Thus, we see that from the descriptive standpoint SPs are identical with volume phases. When coupled with an analysis of the arrangement of adsorbate and substrate atoms from STM patterns, this allows one to construct the crystal lattice model for an SP.

Conductivity of surface phases. With an SP on the surface of silicon, electrical conduction in the near-surface layer can occur through the space-charge region, the SP, and the layer of atoms on the SP [8, 9].

The contribution of the electrical conductivity of a 'silicon – adsorbate' SP to the surface conductivity of silicon with the (100) orientation is estimated as

$$\Delta\sigma = \sigma_s(\mathrm{SP}) - \sigma_s(\mathrm{Si}(100)2\times 1)\,,$$

where σ_s(SP) is the surface conductivity of silicon with a 'silicon – adsorbate' SP and σ_s(Si(100)2×1 is the conductivity of pure silicon with the Si(100)2×1 SP.

The surface-conductivity change measured for the Si(100)2×3-Na SP was found to be negative and equal to $-(1.5\pm 0.8)\times 10^{-5}\ \Omega^{-1}$. The lower surface conductivity of silicon with the Si(100)2×3-Na SP as compared to that of a sample with a pure Si Si(100)2×1 surface may be due to several causes. First, it should be remembered that the alkali metals entering into the composition of an SP may donate valence s electrons to the silicon substrate [10]. In this case, surface states are partially filled up with the 3s electrons of Na atoms, which must result in a decrease in the charge in the near-surface layer and its accumulation between the 'layer' of Na and the uppermost substrate layer of Si. Because of this, conduction through the near-surface layer seemingly must decrease and conduction over the surface (that is, through the Si(100)2×3-Na SP), on the contrary, must increase. However, since the interaction between Na atoms in the SP is weak and the system Na/Si(100) does not possess metallic properties when submonolayer metal coverages (lesser than 1 ML) are used [10], the presence of an Si – Na SP results in a decrease in the value of the surface conductivity as compared to the Si(100)2×1 SP. Besides, surface roughness may affect the conductivity of the Si – Na SP [11].

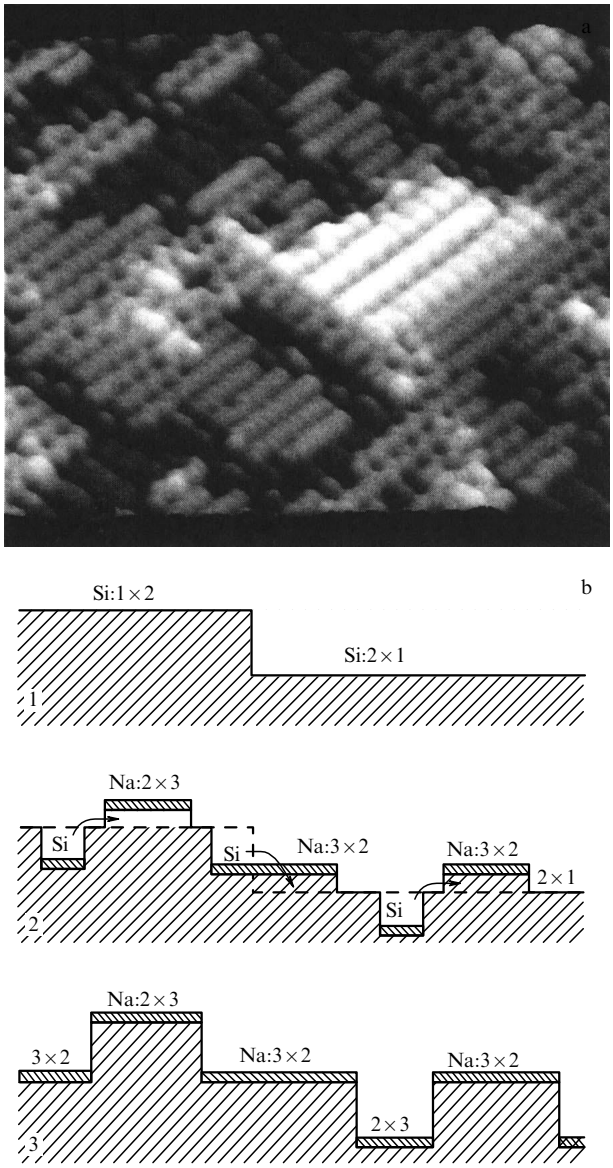

Figure. (a) STM image of a portion of a (100) silicon surface (220×220 A) at the initial stage of the formation of an Si(100)2 × 3-Na surface phase. (b) Schematic representation of the process of the formation of the Si(100)2×3-Na surface phase: (1) Si(100)2×1 terraces separated by monatomic steps before the evaporation of Na; (2) initial stage of the formation of the Si(100)2×3-Na surface phase, arrows show the transfer directions of silicon atoms, dashed line shows the position of the terraces before of Na deposition; (3) completion of the formation of the Si(100)2×3-Na surface phase.

It should be also noted that the formation of other Si – M SPs (for example, Si – Au [8, 9]) leads to an increase in the conductivity as compared to that for a pure silicon surface.

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Scanning tunneling microscopy of 'commensurate – incommensurate' structural phase transitions in the chemisorbed layers of halogens

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The process of chemical interaction of halogens with the surface of metals generally proceeds in two steps: the formation of a monatomic chemisorbed layer in the first stage of the reaction and then, on filling this chemisorbed layer, the formation of a chemical compound proper — metal halogenide. During the formation of a monolayer coating, substrate atoms remain in their crystal lattice, though a strong perturbation of the electron subsystem of the metal takes place, with the resulting occurrence of additional peaks in the local density of electron states in the valence band both below and above the Fermi level [1]. In the second stage of the reaction, metal atoms escape from the substrate lattice and combine with the halogen to form a new chemical compound with its own crystal structure and corresponding spectral features.

Under controlled ultrahigh vacuum conditions, surface chemical reactions have been studied experimentally since the 1970s, that is, since the invention of the first surface analysis methods, i.e., low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) [1 – 3]. The first stage of the reaction under discussion, the formation of a surface lattice by adsorbate, is a process that has been studied comprehensively from the viewpoint of surface crystallography. It was found that the commensurate structures $(\sqrt{3}\times\sqrt{3})$R30° and c(2×2)-Hal formed on the (111) and (110) faces, respectively, and the commensurate structures p(2×2)-Hal or c(2×2)-Hal formed on the (100) face are transformed in a rather complex way as the degree of coating is increased, with all the changes occurring within one monolayer. The complex diffraction pattern obtained for different 'adsorbate/substrate' combinations showed marked distinctions even for the same orientation of the surface. To interpret LEED data, along with the homogeneous isotropic compression model [1 – 4], a model of regular domain walls separating commensurate structure domains was also discussed in the literature [1, 5 – 8]. In the first case all the adsorbate atoms are arranged in an incommensurate uniform lattice, whereas in the second case the only incommensurate atoms are those which are arranged in domain walls. Both surface structures produce the same diffraction patterns [1, 4, 8, 9], which gives no way of determining the actual atomic structure of a surface using diffraction methods only.

In most work on halogen adsorption on metals performed by the LEED method, the first model was taken to be correct. The main argument against the second model is that the interatomic distances in domain walls are too small for the average density of adsorbate atoms observed in experiments. Simple estimates of the interatomic distances gave values which were much less than the van der Waals diameter of a halogen atom, which was believed to be physically impossible [1, 3, 4]. In the case of homogeneous compression, the interatomic distance in the halogen lattice was approximately equal to the van der Waals diameter [1, 3]. Nevertheless, extended X-ray absorption fine structure (EXAFS) measurements show that in some cases the interatomic spacing for halogen atoms within the layer is much less than the van der Waals diameter. For example, in a chromium layer ($R_{vdW} = 3.60$ A) on the (111) or (110) Ag surfaces [10, 11] they were found to be equal to 2.95 A and 3.14 A, respectively. However, to this day no proper explanation has been provided for these data.

The development of local probing microscopy methods with high resolution (up to the atomic level) and their wide use in surface physics and chemistry in the 90s made possible the direct observation of the actual structure of a surface and, hence, allowed one to gain a correct understanding of structural transformations taking place on this surface.

In this report we present images of the actual structure of the Cu(111) surface obtained with atomic resolution at different stages of the formation of chemisorbed chlorine and iodine layers. These images uniquely show that the 'commensurate – incommensurate' structure transition of the $(\sqrt{3}\times\sqrt{3})$R30° → $(n\sqrt{3}\times n\sqrt{3})$R30° type takes place through the formation and evolution of linear domain walls.

All experiments were conducted with the use of an ultrahigh-vacuum four-chamber setup described in detail in Ref. [12]. The setup was equipped with a GPI-300 [1] scanning tunneling microscope, a quadrupole mass spectrometer, an analyzer of the 'cylindrical mirror' type for Auger electron spectroscopy, a three-grid analyzer of electrons for LEED, an ion gun, and a gas-filling system. The base pressure in the setup did not exceed 2×10^{-10} Torr. For preparation of Cu(111) and Ag(111) samples measuring 6×10×2 mm with a surface plane misalignment not worse than 0.5° in ultrahigh vacuum, repetitive cycles of ion etching (Ar^+, 1 keV) and annealing at temperatures of 950 K (Cu) and 850 K (Ag) were used. The concentration of contaminations on a prepared surface did not exceed 1%, as was estimated from AES data. As a result of such preparation, the surfaces obtained provided high-quality (1×1) LEED patterns and STM images with an atomically smooth surface. The adsorption of halogens (chlorine and iodine in molecular form) and STM measurements were carried out at room temperature. To determine the degree of coverage, AES, LEED, thermodesorption mass spectrometry (TDMS), and STM data were

[1] The GPI-300 ultrahigh-vacuum scanning tunneling microscopes are currently manufactured in the Institute of General Physics of RAS.