

Properties of the interaction of europium with Si(111) surface

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Formation of the Eu/Si(111) system as the metal layer thickness gradually increases from 0.5 to 60 monolayers (ML) deposited on the silicon surface at room temperature, and after heating at up to 900 °C, has been studied by Auger electron spectroscopy, electron-energy-loss spectroscopy, and low-energy-electron diffraction. It is shown that room-temperature film growth passes through three stages, depending on the Eu layer thickness: metal chemisorption, interdiffusion of the metal and substrate atoms, and buildup of the metal on the surface of the system. Heating of ultrathin (about one ML) Eu films deposited at room temperature results in ordering of metal atoms on the silicon surface with only weak interaction. Heating thick (above 15 ML) Eu layers on the silicon surface produces silicides whose structure depends on the heating temperature. © 1998 American Institute of Physics. [S1063-7834(98)03703-4]

Rare-earth metals (REM) interacting with a silicon surface produce silicides, which possess a number of unique physicochemical properties, among them an extremely low Schottky barrier (0.3–0.4 eV) at the interface between the REM silicide and *n*-Si surface, fairly high electrical and heat conductivity, and comparatively low formation temperature.^{1–3}

The present work studies the interaction of Eu with the silicon surface. Eu is normally in the divalent state and retains it in interaction with silicon, whereas when bound in a chemical compound its behavior resembles that of *s* metals. In this it differs from most REMs. The present study focuses primarily on the electronic and crystalline structures of systems consisting of a thin Eu layer on the Si(111)7×7 surface in their dependence on the annealing temperature and metal-layer thickness. The electronic structure of these systems was investigated by Auger electron spectroscopy (AES) and electron-energy-loss spectroscopy (EELS), and the surface crystalline structure, by low-energy electron diffraction (LEED).

1. EXPERIMENTAL TECHNIQUES

The studies presented in this work were carried out *in situ* in an ultrahigh vacuum at $(1-2) \times 10^{-10}$ Torr. The sample was a $7 \times 5 \times 0.2$ -mm plate of As-doped *n* silicon with a resistivity of $0.002 \Omega \cdot \text{cm}$, with a polished (111) face. Eu was deposited by evaporation from a quartz crucible. The flux deposited onto the Si surface was monitored by means of a quartz piezomicrobalance. The sample was directly heated by passing dc current through the silicon plate. The heating temperature was determined by the magnitude of the current through the sample. The correspondence between the current and the heating temperature was verified in preliminary calibration experiments by means of an optical pyrometer. The silicon surface was cleaned by a brief high-temperature annealing at about 1100 °C. The cleanliness and

crystalline perfection of the Si(111)7×7 surface in the course of experiments were monitored by AES and LEED.

The Auger and EEL spectra were obtained with a four-grid hemispherical retarding-field electron analyzer with an energy resolution of 0.25% and an electron beam normally incidence onto the sample. The analyzer design permitted observation of the LEED patterns as well. The analyzer and setup design are described in detail elsewhere.⁴ The Auger spectra presented in this work were taken in the dN/dE mode at 1-keV primary-electron energy. The EEL data were measured in the dN/dE mode at the primary electron energy of 200 eV and subsequently processed to yield d^2N/dE^2 spectra.

2. EXPERIMENTAL RESULTS

Figure 1a shows some Auger spectra of the Eu/Si(111) system for different Eu-layer thicknesses (1, 7, 15, and 60 ML, with 1 ML $\approx 3.8 \text{ \AA}$) deposited on the Si surface at room temperature, and an Auger spectrum of a clean Si(111)7×7 surface, obtained in the kinetic energy interval of 60 to 150 eV. This energy interval permits one to observe simultaneously in the spectra the Si $L_{23}VV$ peak at about 92 eV and Auger peaks of europium at 82 eV (due to the $N_1N_{45}N_{45}$ and $N_{45}O_{23}O_{23}$ transitions), at about 103 eV (originating from the $N_{45}O_{23}N_{67}$ and $N_{45}O_{23}V$ Auger transitions), to be called in what follows the *NON* peak, the $N_{45}N_{67}N_{67}$ Auger peak at 122 eV, and peaks at 129 and 135 eV caused by hole recombination between the $4d$ and $4f$ levels. In describing the processes occurring in the Eu/Si(111) system, we shall subsequently focus attention primarily on the *NON* peak of Eu, because it is the strongest of all Eu Auger peaks and provides information on the valence band. A comparison of the spectra in Fig. 1a shows that the amplitude of the Eu $N_{45}O_{23}N_{67}$ peak grows, and that of the silicon $L_{23}VV$ peak, gradually decrease with increasing Eu layer thickness. The silicon peak at 91.5 eV shifts by about 0.6 eV toward lower kinetic energies even at coverages of one monolayer, and

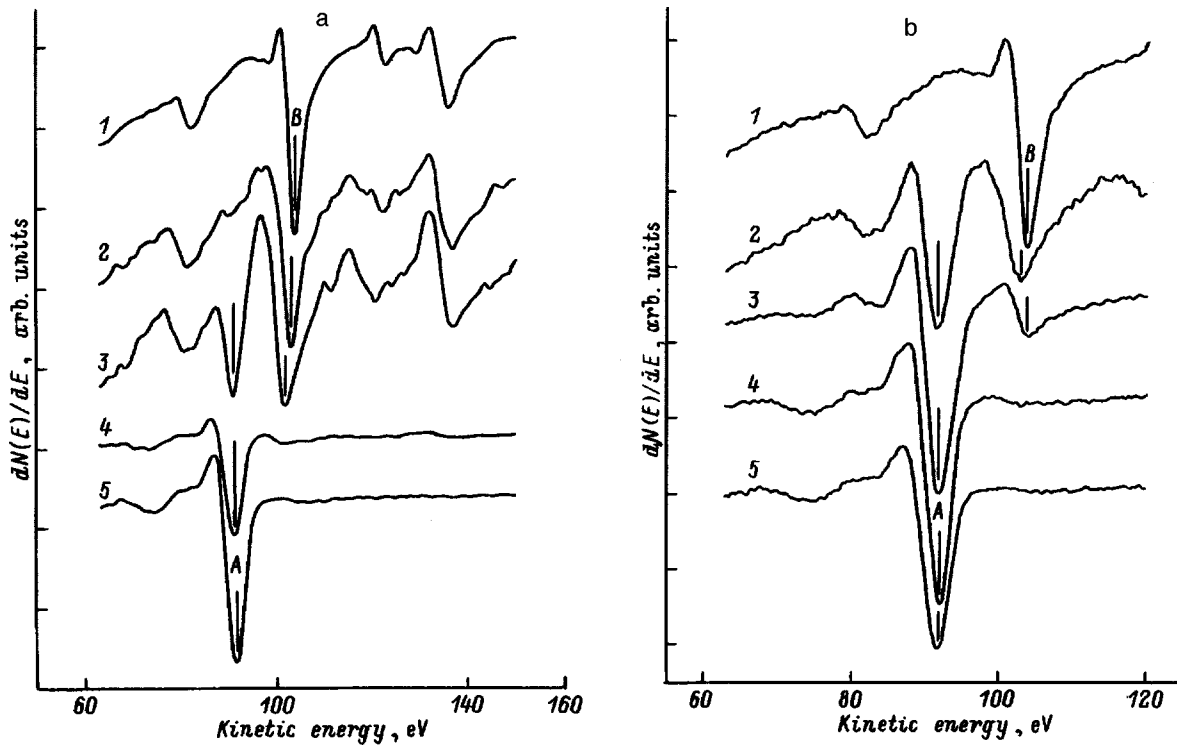


FIG. 1. Auger spectra of the Eu/Si(111) system. (a) Spectra obtained from Eu layers with different thicknesses deposited with $E_p = 1$ keV at room temperature (ML): 1—60, 2—15, 3—7, 4—1, 5—clean Si(111)7x7 surface; A-Si $L_{23}VV$ peak ($E = 91.8$ eV), B-Eu $N_{45}O_{23}N_{67}$ peak ($E = 103$ eV). (b) Spectra obtained after the heating of Eu layers with different thicknesses deposited at room temperature ($E_p = 1$ keV): 1—60 ML without heating, 2—15 ML, heating at 400 °C; 3—15 ML, heating at 700 °C (2x2 structure); 4—1 ML, heating at 500 °C (3x1 structure); 5—clean Si(111)7x7 surface; A-Si $L_{23}VV$ peak ($E = 91.8$ eV), B-Eu $N_{45}O_{23}N_{67}$ peak ($E = 103$ eV).

does not change position with further deposition of europium. The Eu peak at ≈ 103 eV shifts gradually toward higher kinetic energies with increasing thickness of the deposited layer. The relative change in amplitude of the Si $L_{23}VV$ peak (Fig. 2a) and of the Eu $N_{45}O_{23}N_{67}$ peak (Fig. 2b) with increasing metal-layer thickness permits one to follow the change in intensity of individual Auger peaks in more detail. The Auger peak amplitude was determined from the intensity change between the low- and high-energy extrema of the corresponding Auger dN/dE peaks. In Fig. 2a, the 100%-level is the amplitude corresponding to the $L_{23}VV$ peak from clean silicon surface, and in Fig. 2b, that of the NON Eu peak for the 15-ML thick metal layer on Si surface. We see that the amplitudes of the Auger peaks under study vary nonuniformly with Eu layer thickness. The sharpest changes occur at metal layer thicknesses below 2 ML.

Figure 3a presents EEL spectra in the form $d^2N(E)/dE^2$ for the Eu/Si(111) system for metal layers four and 30 monolayers thick deposited at room temperature, and for a clean Si surface. The characteristic features of these spectra are the plasma loss peaks in silicon and europium (about 17.7 and 9 eV, respectively) and the Eu $5p$ EEL feature (at ≈ 25 eV). We readily see that the Eu EEL spectrum undergoes substantial changes even at $\theta = 4$ ML. The silicon plasma-loss peak (17.7 eV) practically disappears against the background of the features associated with losses in the metal (core-level Eu $5p$ and plasma losses in europium at 8 eV) and a new peak at 12.5 eV. The EEL spectrum obtained from 30 monolayers of Eu exhibits a substantial increase in the Eu plasma loss

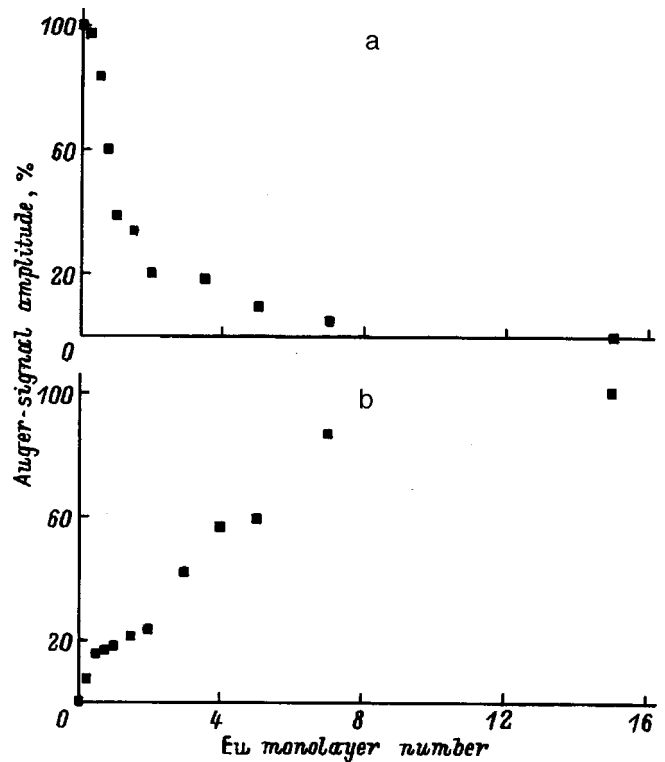


FIG. 2. Relative variation of the amplitude of (a) Si $L_{23}VV$ peak and (b) Eu $N_{45}O_{23}N_{67}$ peak with increasing thickness of Eu layer deposited at room temperature.

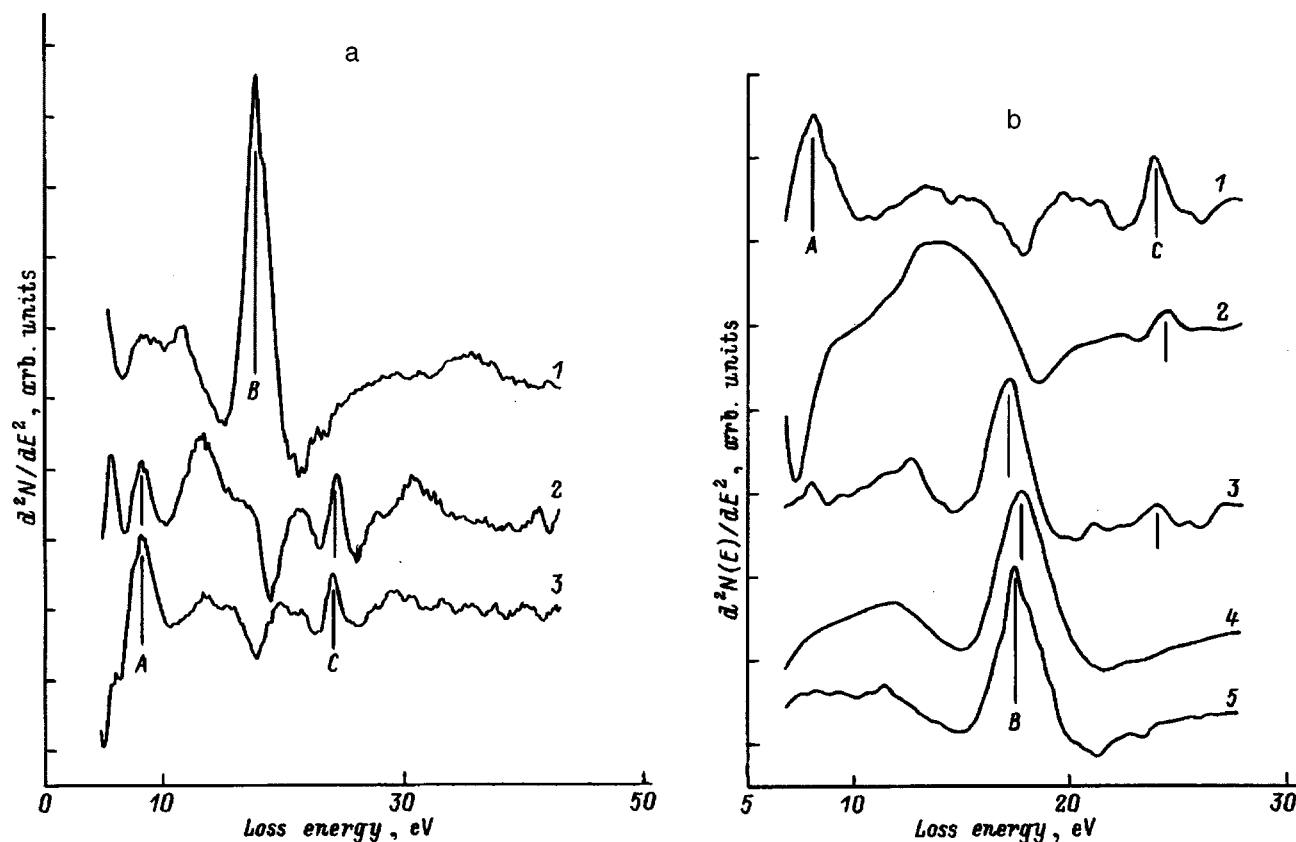


FIG. 3. EEL spectra of Eu/Si(111) system. (a) Spectra obtained from different thicknesses of Eu layer deposited with $E_p=200$ eV at room temperature. 1—clean Si(111)7×7 surface, 2—four Eu ML, 3—30 Eu ML, A—Eu plasma loss peak ($\hbar\omega=8.1$ eV), B—Si bulk plasma loss peak ($\hbar\omega=17.6$ eV), C—Eu 5p loss peak ($E=24.5$ eV); (b) Spectra obtained after the heating of Eu layers with different thicknesses deposited at room temperature ($E_p=200$ eV): 1—30 ML without heating, 2—15 ML, heating at 400 °C; 3—15 ML, heating at 700 °C (2×2 structure); 4—1 ML, heating at 500 °C (3×1 structure); 5—clean Si(111)7×7 surface; A—Eu plasma loss peak ($\hbar\omega=8.1$ eV), B—Si bulk plasma loss peak ($\hbar\omega=17.6$ eV), C—Eu 5p loss peak ($E=24.5$ eV).

peak and Eu 5p excitation loss feature, with the latter shifting by approximately 0.5 eV toward lower binding energies compared to a thin Eu layer on Si.

The Eu/Si(111) system produced by heating at different temperatures was studied with thin (1–2 ML) and thick (15 and 60 ML) Eu layers deposited at room temperature. It was established that the geometric and electronic structures of the systems forming after the heating of thick metal layers differ negligibly. The structure of these systems depends on the heating temperature. Figure 1b displays the most characteristic Auger spectra obtained after heating at different temperatures of a system consisting of 15 monolayers of Eu on a Si(111)7×7 surface. Also shown is an Auger spectrum of the system produced by heating one monolayer of the metal at a temperature of about 400 °C.

As follows from LEED patterns, structures with an ordered crystalline surface form only at sufficiently high heating temperatures (above 600 °C). It was established that systems prepared at heating temperatures of 700 and 800 °C are characterized by 2×2 and 3×3 ordered structures relative to silicon, respectively. In the case of the 2×2 structure the stoichiometry of the compound was tentatively estimated as $\text{EuSi}_{2.2}$. The estimate was made by comparing the silicon and europium Auger peak amplitudes in the spectra obtained.

Figure 3b shows EEL spectra of the same phases as in Fig. 1b. These spectra are dominated by a silicon plasma-loss

peak shifted slightly toward lower binding energies. One also sees clearly in the spectrum of the 2×2 structure a feature at 13 eV.

An analysis of the compounds formed after the heating of the Eu/Si(111) system revealed that those that appear at relatively low temperatures are metastable; indeed, the composition and electronic structure of the surface change with time. For instance, while immediately after heating at $T \approx 400$ °C silicon is detected in considerable amounts on the surface (see Fig. 1b), after 12 hours of keeping the system at room temperature the Si $L_{23}VV$ Auger peak practically disappeared. Repeated heating, both at the same and at higher temperatures, up to 500 °C, does not affect the spectrum, which implies that the system thus formed is stable.

Studies of systems produced by heating one monolayer of europium on silicon surface showed that a number of ordered structures form there. When heated at $T \approx 400$ °C, the structure forming on the surface is 5×1, at higher temperatures (about 500 °C) it is 3×1, and for $T > 700$ °C, it is the 1×1 structure, which transforms gradually with increasing heating temperature to the 7×7 superstructure characteristic of clean Si surface. No such structures were observed when heating thick metal layers. The Auger spectrum of the 3×1 phase is shown in Fig. 1b, and the EEL spectrum is shown in Fig. 3b together with spectra of the systems produced by heating a thick Eu layer on the Si surface.

3. DISCUSSION OF RESULTS

The mechanisms of Eu film growth on Si surface can be analyzed by considering the dependences of the amplitudes of the most characteristic Eu and Si Auger peaks on the metal layer thickness displayed in Fig. 2a,b. We readily see that these graphs are nonmonotonic, with the slopes changing at a thickness of about two monolayers. This behavior implies that Eu films of different thickness grow by different mechanisms. For small thicknesses, the curves, on the whole, correspond to monotonic growth of Eu films on Si(111). Eu atoms start to interact with the substrate even at submonolayer coverages, which is implied by the shift of the Si $L_{23}VV$ peak at these thicknesses toward lower kinetic energies (Fig. 1a), and this shift is most likely connected with a charge transfer from Eu to Si atoms. This observation is in accord with the conclusions of Ref. 5.

As seen from Fig. 2, as the Eu film thickness increases above two monolayers, the rates of decrease of the silicon Auger peak amplitude and of the increase of the europium Auger peak amplitude slow down noticeably, which suggests a change in the pattern of interaction with the substrate. This behavior for Eu coverages with $\theta > 2$ can be identified with one of the two growth mechanisms, namely, the Stransky–Krastanov mechanism, involving formation of three-dimensional clusters on a uniform adsorbate layer, or the interdiffusion mechanism, where, starting with a certain adsorbate layer thickness, atoms of the substrate mix with those of the adsorbate, a process accompanied by breaking of atomic bonds in the upper layers of the substrate. In our case, the Si $L_{23}VV$ peak in the Auger spectrum was clearly seen even with Eu thicknesses above ten monolayers, whereas the silicon plasma loss peak disappeared from the EEL spectrum at a Eu film thickness of just four monolayers (Fig. 3a), which implies destruction of the energy bands formed by silicon atoms as a result of the rupture of Si–Si chemical bonds. This argues for the second, interdiffusion mechanism.

As evident from Fig. 2a, for Eu layers more than 7–10 ML thick, the $L_{23}VV$ peak of silicon practically disappears from the spectra. Starting from these thicknesses, further deposition leads to a buildup of Eu, and the surface structure acquires the features of a metallic Eu phase, which is indicated by the fact that the Auger spectrum of the system formed after deposition on the Si surface of a thick Eu layer (Fig. 1a) coincides with that of the metallic Eu phase.⁶

The above analysis implies that room-temperature formation of the Eu/Si(111) system passes through the following three stages: (1) For coverages less than two monolayers, Eu spreads uniformly over the silicon surface, and interaction of Eu atoms with the substrate becomes manifest already in this stage; (2) For Eu thicknesses above two monolayers, the bonds coupling silicon atoms in the near-surface layers of the substrate break, thus making possible interdiffusion of europium and silicon atoms; (3) For coverages exceeding 7–10 ML, europium starts to build up on the silicon surface.

Heating a thick layer of Eu on the surface of Si at high enough temperatures causes compounds with an ordered structure to form on the surface. An analysis of LEED patterns shows the formation on the surface at $T \approx 700$ °C of a

2×2 structure, and at $T \approx 800$ °C, of a 3×3 structure. As seen from Fig. 3b, the spectrum of the 2×2 EEL phase exhibits a noticeable shift of the silicon plasma loss peak and a feature in the region of 13 eV. This shows that Eu atoms interact with atoms of the substrate and become chemical bound. The Auger spectrum of this phase (Fig. 1a) permits certain conclusions on the character of this bonding. We see that the Si Auger peak does not change its position relative to the spectrum of the clean substrate, which suggests that this peak returned to its original position (as mentioned earlier, its energy changed in the course of room-temperature growth). One may thus conclude that there is no noticeable charge transfer between Si and Eu atoms in the systems formed after the heating. It follows that the bonding between atoms in this system is probably mostly covalent. This evidence gives credence to the assumption that the 2×2 and 3×3 structures relate to epitaxial silicides. For the 2×2 structure, the composition of this compound can be described by an approximate formula $\text{EuSi}_{2.2}$, which is in agreement with the reported silicide.^{5,7}

Heating at $T \approx 400$ °C of a thick Eu layer deposited at room temperature on Si(111) produces a system with a high Si concentration on the surface (Fig. 1b) which does not generate any LEED pattern. When stored at room temperature, this system exhibits a decrease in the Si concentration on the surface, until it disappears completely in 12 h, as evidenced by the absence of the Si Auger signal in the spectra. Subsequent heating of the system up to $T \approx 500$ °C did not change the spectra noticeably.

It can be suggested that when a thick Eu layer on Si(111) is heated at $T \approx 400$ °C, Si atoms diffuse through the Eu layer toward the surface. The conditions on the surface are, however, not conducive to formation of strong chemical bonds between Si and Eu atoms, and therefore the excess of Si drifts away in time to become bonded at the interface separating europium and silicon, where a layer forms which precludes further Si diffusion to the surface in subsequent heatings.

Heating an ultrathin (one monolayer-thick) Eu film does not introduce any serious distortions into the silicon surface structure also, but gives rise to the formation of compounds with an ordered surface structure. As the temperature increases, 3×1 and 5×1 patterns appear. The 3×1 phase formed at a temperature of about 400 °C. The Auger and EEL spectra of this surface are shown in Figs. 1b and 3b, respectively. This system differs most significantly from those corresponding to bulk epitaxial silicides in the crystal-line structure of the surface and a lower temperature of formation of the ordered surface structure. As seen from the Auger spectrum, formation of this system does not result in a shift of the Si $L_{23}VV$ peak toward lower kinetic energies, which was observed before the heating. Moreover, a more careful analysis of the spectrum revealed a reverse shift of the peak by about 0.4 eV, which indicates interaction between Eu and Si atoms different in character from that characteristic of bulk silicides. The EEL spectrum of the 3×1 surface is very close in shape to that of clean silicon surface. This suggests that the surface did not experience any destruc-

tive action from the side of the adsorbate. It may be conjectured that formation of ordered structures after heating of thin Eu layers on Si(111) does not involve destruction of Si–Si bonds in near-surface layers. In contrast to systems produced in the heating of thick Eu layers, europium atoms become distributed uniformly over silicon surface after the film heating and occupy preferred positions, in which they form strong, predominantly covalent chemical bonding with silicon atoms involving weak electron density transfer between the two species.

The results obtained in this work can be summed up as follows.

1. Eu atoms deposited on the Si(111) surface at room temperature interact with the substrate in three stages, depending on the actual metal layer thickness:

a) for Eu coverages below two monolayers, monotonic film growth on silicon surface, with no bonds between Si atoms in the upper layers being broken;

b) for Eu coverages from two to seven monolayers, mixing (interdiffusion) of Eu atoms with atoms in the topmost layers of the silicon substrate, which is accompanied by breaking of silicon bonds;

c) for thicknesses above 7–10 monolayers, metal buildup on the surface and formation of a solid metal layer as Eu deposition is continued.

2. Heating thick (above 15 ML) Eu layers at temperatures from 600 to 800 °C produces epitaxial europium silicides on the surface, with the structure and composition depending on the heating temperature. In particular, phases with 2×2 and 3×3 surface patterns were observed. Chemical interaction between Eu and Si atoms in these structures has a primarily covalent character.

3. Heating a thick Eu layer at temperatures of about 400 °C forms a metastable system, whose surface immedi-

ately after the heating is enriched in Si atoms. When maintained at room temperature, silicon atoms diffuse into the bulk and stabilize the interface. Repeated heating of the system after a considerable time (above 12 h) does not reproduce the effect, in other words, with time the system reaches a stable state.

4. Heating ultrathin (about one monolayer) Eu layers produces ordered structures on the surface different from those of epitaxial silicides. The differences consist in a lower formation temperature of the ordered structures (about 400 °C) and in the crystalline structure of the surface (one observed 3×1 and 5×1 surface structures). These structures form in the reconstruction of the Si(111) surface under a uniform flux of adsorbing Eu atoms.

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