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**LOW-DIMENSIONAL SYSTEMS  
AND SURFACE PHYSICS**

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# Interaction of Thin Silicon Layers with the (0001) Surface of Rare-Earth Metals

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**Abstract**—The electronic and crystalline structures of the systems formed upon deposition of silicon layers onto the Gd(0001) and Dy(0001) surfaces of single-crystal films annealed subsequently at  $T = 450\text{--}500^\circ\text{C}$  have been studied by low-energy electron diffraction (LEED) and also by the Auger electron and angle-resolved photoelectron spectroscopy of the valence band and the Si(2*p*) core level. It is shown that the systems thus produced can be described as starting single-crystal films of Gd and Dy, with 3D islands of the silicides of these metals on the surface of the corresponding metal films. © 2000 MAIK “Nauka/Interperiodica”.

## 1. INTRODUCTION

At present, there is a wealth of publications on the interaction of rare-earth metals (REM) with silicon surface. It is reliably established that the REM deposition onto the Si(111) surface followed by annealing at a temperature of  $\sim 400\text{--}500^\circ\text{C}$  gives rise to a strong interaction of Si with the rare-earth metals and epitaxial growth on the surface of ordered layers of REM disilicides with an  $\text{AlB}_2$ -type structure and a stoichiometry close to  $\text{MeSi}_{1.7}$  [1–9]. These disilicides have a layered Si–REM–Si structure with a hexagonal arrangement of Si and REM atoms inside the corresponding layers [1, 5–9]. Note that if rare-earth metal atoms form centered hexagons (i.e., with an atom at the hexagon center) with a lattice constant of  $\sim 3.8 \text{ \AA}$ , the silicon atoms inside the corresponding layers build noncentered graphite-like hexagons with one additional vacancy in each hexagon [1, 2, 6–8]. These vacancies form, in turn, an ordered structure of a larger size whose diffraction patterns are of the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  type with respect to the principal structure. These vacancies account for the silicon hexagon matching to the corresponding basal lattice constant of the system ( $\sim 3.8 \text{ \AA}$ ). It is this that stimulates the growth of epitaxial layers of nonstoichiometric REM disilicides on the Si(111) surface with a good lattice match between the disilicide film and the silicon substrate. This work was aimed at studying the interaction between silicon and rare-earth metals (Gd, Dy) in a Si/REM system obtained by deposition of silicon onto an REM surface, which can be called “reverse” with respect to the system formed by REM deposition on the silicon surface.

We studied the electronic and crystalline structure of the systems produced by deposition of thin silicon

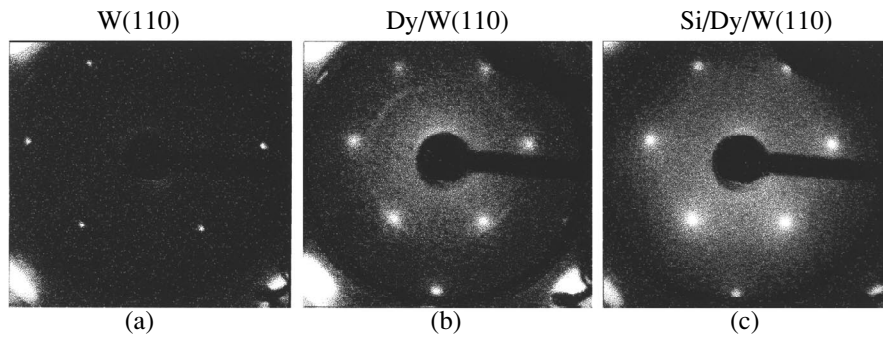
films onto the (0001) surface of the gadolinium and dysprosium single-crystal films grown on a W(110) single-crystal surface. The basal constants of the crystal structure of these rare-earth metals are smaller than those of the epitaxial silicides in the “direct” system:  $3.63 \text{ \AA}$  for Gd and  $3.59 \text{ \AA}$  for Dy [10]. On the one hand, this removes the requirement of lattice matching between the silicide phases and the REM substrate. On the other, these metals readily form silicide-like structures in the direct system; i.e., when a rare-earth metal is deposited onto the Si(111) surface with its subsequent thermal annealing [3, 4, 11, 12].

In this work, the studies were carried out by the methods of Auger electron and photoelectron spectroscopy of the valence band and the Si(2*p*) core level in the course of deposition of thin Si layers on the (0001) surface of Gd and Dy single-crystal films, followed by thermal annealing at  $\sim 450\text{--}500^\circ\text{C}$ . Low-energy electron diffraction (LEED) spectroscopy was employed to characterize the crystal structure of the systems.

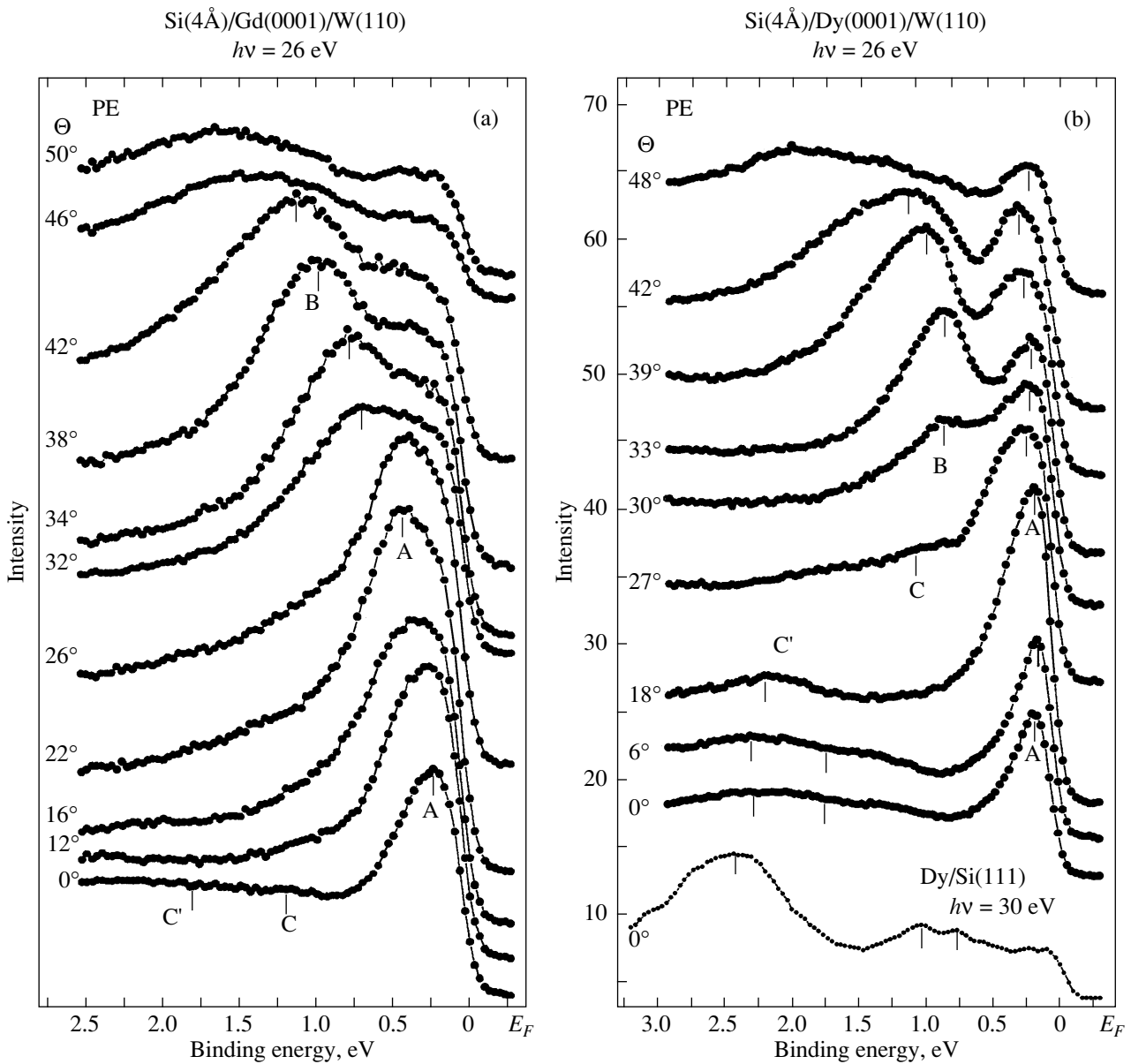
It was shown that the systems formed by deposition of silicon thin layers on the (0001) surface of the gadolinium and dysprosium single-crystal films annealed subsequently at  $\sim 450\text{--}500^\circ\text{C}$  can be described as single-crystal films of rare-earth metals (Gd, Dy) with 3D islands of the silicides of these rare-earth metals created on the surface of the system.

## 2. EXPERIMENTAL TECHNIQUE

The photoelectron studies were carried out at the Synchrotron Radiation Center (BESSY I, Berlin) on the TGM-3 channel with the use of a WSW-ARIES-type electron spectrometer capable of angular resolu-



**Fig. 1.** LEED patterns ( $E_p \sim 83$  eV) for (a) clean W(110) surface, (b) Dy(0001) single-crystal film on the W(110) surface, and (c) Si(12 Å)/Dy(0001)/W(110) system after annealing at 450–500°C.



**Fig. 2.** Valence-band photoelectron spectra for different photoelectron polar takeoff angles ( $\Theta$ ) measured for the systems (a) Si(4 Å)/Gd(0001)/W(110) and (b) Si(4 Å)/Dy(0001)/W(110) after annealing at 450–500°C. Shown in the bottom of Fig. 2b is the photoelectron spectrum of the Dy/Si(111) system after annealing at 400–500°C.

tion and provided with a LEED diffractometer. The total energy resolution of the system during experiments was no worse than 0.2 eV. We measured the photoelectron spectra of the valence band and the Si(2*p*) core level in the course of deposition of silicon thin films of different thicknesses onto the (0001) surface of the gadolinium and dysprosium single-crystal films, followed by warming the systems up to temperatures of 450–500°C. The exciting photon energy was chosen so as to reduce the contribution of the REM 4*f* and 5*d* states to the valence-band photoelectron spectra and was equal to 26 eV. The Si(2*p*) photoelectron spectra were measured at an incident energy of 130 eV, which provided the maximum possible surface sensitivity of the experiment. The Auger electron spectra of the Si/REM systems studied during the Si deposition and thermal annealing were measured by means of a four-grid retarding-field energy analyzer at a primary-electron energy of ~1 keV.

The gadolinium and dysprosium single-crystal films were grown on the (110) surface of a tungsten single crystal according to the standard procedure [13, 14] by depositing these metals to a thickness of ~150–200 Å, followed by thermal annealing at a temperature of ~400–500°C. The films thus prepared had a hexagonal structure characteristic of the REM(0001) surfaces. The diffraction patterns obtained from a clean W(110) surface and a dysprosium single-crystal film grown on the W(110) surface are compared in Figs. 1a and 1b, respectively. The LEED patterns of a gadolinium single-crystal film were similar. Silicon was deposited onto the REM films from a silicon plate heated directly by passing through it electric current. The thickness of the deposited Si and REM layers was determined from the frequency shift of a quartz resonator placed inside the chamber so as to be at the same conditions as the sample. The base pressure in the chamber during the experiment was no higher than  $1 \times 10^{-10}$  Torr. After the silicon deposition, the Si/Gd(0001) and Si/Dy(0001) systems were annealed at 450–500°C. As a result of this treatment, both systems recovered the hexagonal-structure LEED patterns characteristic of the original surfaces of the gadolinium and dysprosium single-crystal films. Figure 1c shows a typical LEED pattern for the Si/Dy(0001) system after its annealing at 450–500°C. Similar patterns were observed for the Si/Gd(0001) system.

### 3. RESULTS AND DISCUSSION

Figures 2a and 2b present the photoelectron spectra of the valence band near the Fermi level at different polar photoelectron takeoff angles for the Si(4 Å)/Gd(0001) and Si(4 Å)/Dy(0001) systems after annealing at 450–500°C. [The spectra of thicker (up to 12 Å) predeposited Si layers measured after thermal annealing had the same pattern.] The photoelectron spectra of both systems were

measured along the  $\Gamma$ –*M*– $\Gamma$  direction of the surface Brillouin zone of the rare-earth metal. As is seen from Figs. 2a and 2b, the photoelectron spectra obtained for polar angles below 30° relative to the normal to the surface for both systems have a strong feature (*A*) in the range of binding energies near the Fermi level (0–0.5 eV). The structure of the spectra changes with an increase in the polar angle. The *A* feature first shifts toward higher binding energies and, at polar angles above 30°, splits into two features (*A* and *B*), one of which (*B*) strongly disperses toward higher binding energies. The *A* structure near the Fermi level is more complex. However, one can likewise isolate here features dispersing with a variation in the polar angle and reaching a maximum binding energy at polar angles of ~25 and 50°. The above variations in the binding energy within the main electron groups (features) in the valence band of the Si/Gd(0001) and Si/Dy(0001) systems after annealing are shown graphically in more detail in Figs. 3a and 3b, which display the dispersion relations  $E(k_{\parallel})$  derived from the photoemission spectra with the use of the standard expression

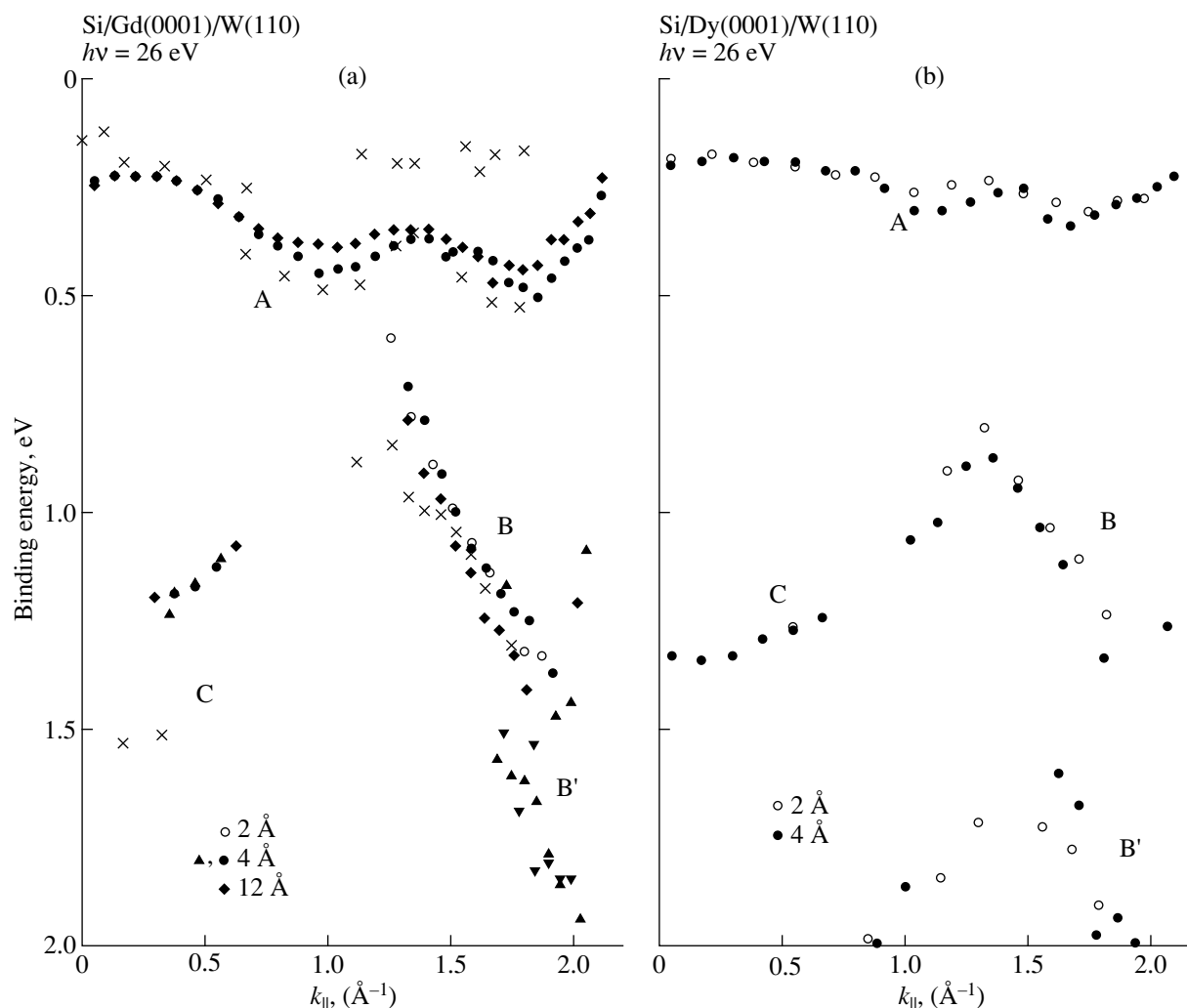
$$k_{\parallel} \sim 0.51 \sqrt{E_{kin}} \sin \Theta,$$

where  $k_{\parallel}$  is the parallel component of the quasi-momentum in the Brillouin zone,  $E_{kin}$  is the photoelectron kinetic energy, and  $\Theta$  is the photoelectron polar takeoff angle relative to the surface normal.

The features corresponding to different thicknesses of the predeposited silicon layers (2, 4, and 12 Å) are identified in Figs. 3a and 3b by different symbols. For comparison, crosses in Fig. 3a show the corresponding dispersion relations for the original Gd(0001) single-crystal film, which were measured in this work also for  $h\nu = 26$  eV.

For comparison, Fig. 2b presents a photoelectron spectrum of epitaxial Dy disilicide obtained in the direct system by depositing Dy onto the Si(111) surface, with its subsequent annealing at ~500°C. This spectrum exhibits a clearly pronounced silicide-like structure with the main features at binding energies of 0.8, 1.1, and about 2.5 eV—a pattern similar to that of the valence band of the disilicides of other rare-earth metals, including Gd [3–8]. As is seen from comparison with the spectrum of dysprosium silicide, the Si/Dy(0001) system does not exhibit distinct spectral features characteristic of epitaxial bulk phases of REM disilicides. One can distinguish only very weak features near the binding energies of 2–2.5 and 1–1.5 eV (*C* and *C'*), which are identified in the figure by dashes.

The photoelectron spectra of the Si/Gd and Si/Dy systems presented in Figs. 2a and 2b resemble more closely those of the valence band, which are characteristic of the original Gd(0001) and Dy(0001) single-crystal films. A comparison with the dispersion relations obtained for a clean Gd(0001) surface shows that



**Fig. 3.** Dispersion relations of the main valence-band features in the  $\Gamma$ - $M$ - $\Gamma$  direction of the surface Brillouin zone of rare-earth metals for the systems (a) Si/Gd(0001)/W(110) and (b) Si/Dy(0001)/W(110) after annealing at 450–500°C. The different symbols identify the Si layer thicknesses. For comparison, crosses in Fig. 3a show the dispersion relations of the ground electronic states for a clean Gd(0001)/W(110) film.

the main features in the electronic structure of the Gd(0001) film and the Si/Gd(0001) system after annealing are clearly similar to each other. This relates primarily to the *B* feature, which disperses strongly toward higher binding energy for polar angles  $\Theta > 25$ – $30^\circ$  ( $k_{||} > 1$ – $1.2 \text{ \AA}^{-1}$ ). The pattern of the variation and the binding energies of the main features (*A* and *B*) in the valence band of the original Gd(0001) film and the Si/Gd(0001) system after annealing practically coincide.

The variations in the photoelectron spectra and in the binding energies for the main valence-band features (*A*, *B*, and *C*) of the Si/Gd and Si/Dy systems presented here correlate with the theoretical and experimental studies made for the Gd(0001) and Dy(0001) surfaces in the  $\Gamma$ - $M$ - $\Gamma$  direction [13–17]. This provides support for the above assumption that the main features in the

photoelectron spectra characteristic of the starting Gd(0001) and Dy(0001) single-crystal films are retained after deposition of thin silicon layers, which are subsequently annealed at 450–500°C.

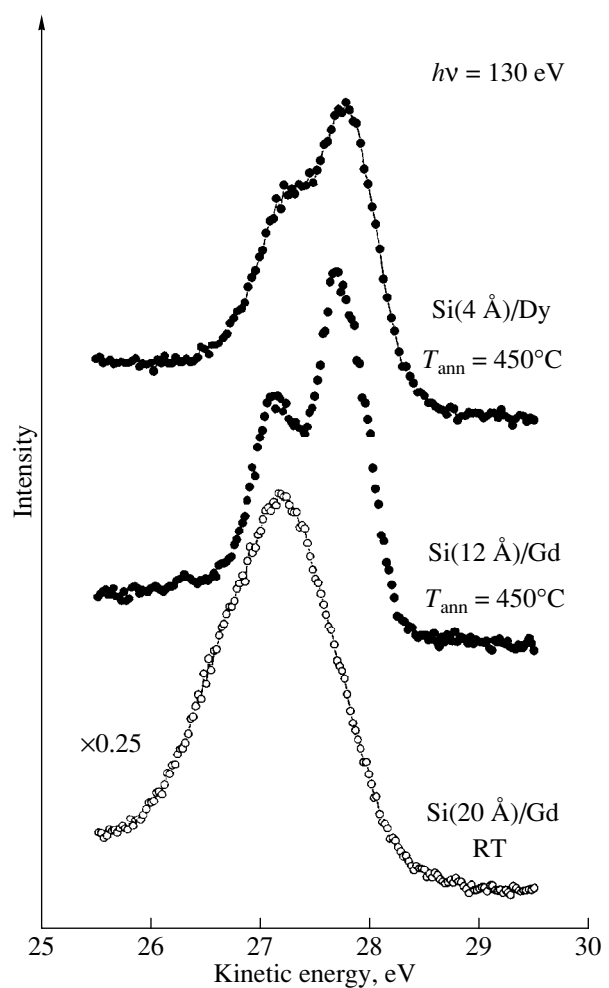
Figure 4 displays the Si(2*p*) core-level photoelectron spectra measured for the Si(12 Å)/Gd(0001) and Si(4 Å)/Dy(0001) systems after annealing at  $\sim 450$ – $500^\circ\text{C}$ . Also shown for comparison is a photoelectron spectrum for a  $\sim 20$ -Å-thick silicon layer deposited onto a Gd film and measured directly after a room-temperature deposition of silicon. An analysis of the spectra permits the following conclusion. If a spectrum obtained before the annealing of the system has a single broad peak with a maximum at a kinetic energy of  $\sim 27.2$  eV, the annealing leads to the formation of a distinct Si(2*p*) doublet and a shift of the spectrum as a whole toward higher kinetic energies (and, hence, toward lower binding energies). After the annealing of

the Si/Dy system, one can observe a similar Si(2*p*) doublet at the same energies (with one peak at about 27.3 eV, and another, at ~27.8 eV). The energies of the peaks in the doublet do not depend on the thickness of the predeposited silicon layer. At the same time, the location of the maximum of the Si(2*p*) peak before the annealing of the system does depend on the thickness of the Si layer deposited preliminarily and varies from 27.5 to 26.8 eV for the thicknesses studied in the work (from 2 to 20 and 50 Å). Following the annealing of the Si/Gd and Si/Dy systems, the intensity of the Si(2*p*) peak decreases substantially.

Figures 5a and 5b demonstrate the variations in the silicon and rare-earth metal (Gd, Dy) Auger spectra obtained after the deposition of silicon layers with the different thicknesses (3, 12, and 15 Å) on the Gd(0001) and Dy(0001) surface and annealing of the Si/REM systems with the different thicknesses of the deposited Si layer at a temperature of 450–500°C. Analysis of the spectra shows that the Si(LVV) Auger peaks before and after the annealing differ substantially in shape. While before the annealing (particularly in the case of the 50-Å-thick silicon layer), the Si(LVV) Auger peak is close in structure to that characteristic of pure noninteracting silicon, after the annealing, this peak has a structure observed in direct systems upon formation of the bulk REM silicides [12, 18], particularly the Gd silicide [12].

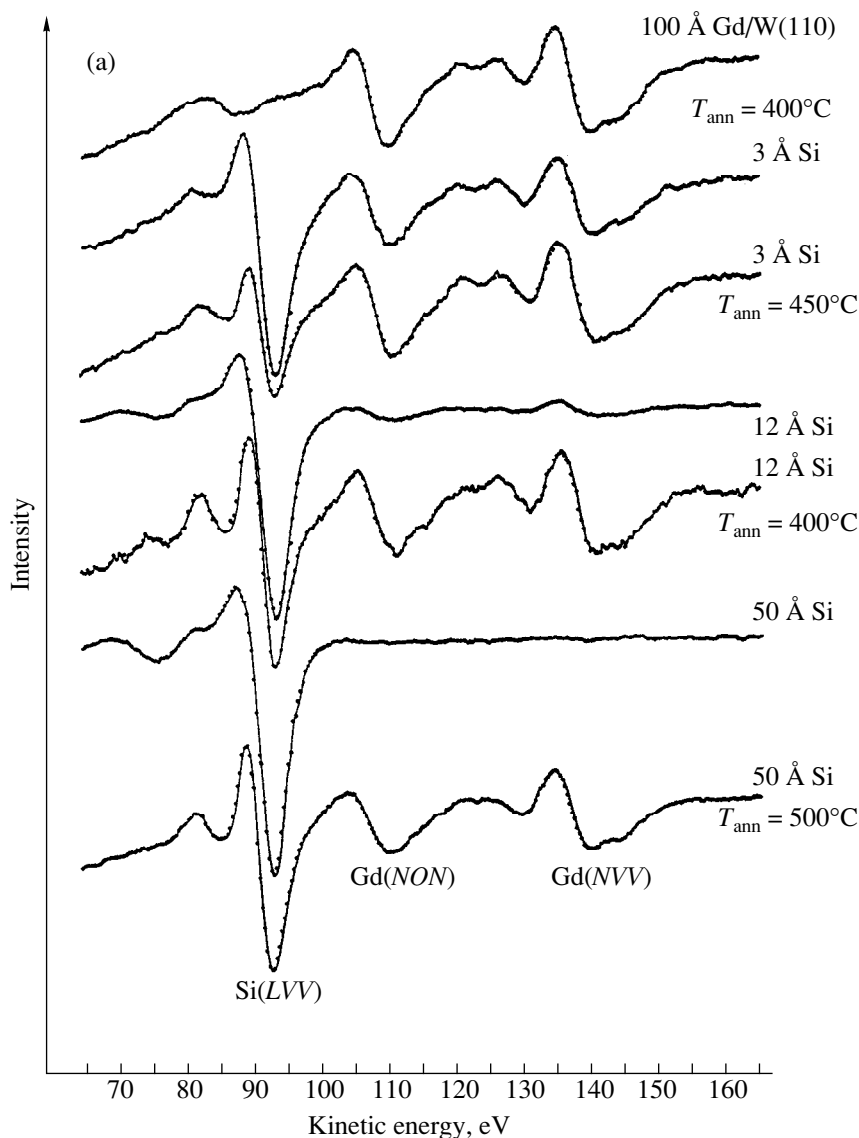
Thus, analysis of the Si(2*p*) photoelectron spectra and the Si(LVV) Auger electron spectra evidences the presence of silicon on the surface of REM films after the silicon deposition and following their heating despite the fact that the valence band manifests itself primarily in the features typical of REM films. The location of the Si(2*p*) doublet and its structure are similar to those of the features in the Si(2*p*) spectra of REM silicides [3–6]. The Si(LVV) Auger electron spectra obtained after the annealing of the Si/Gd and Si/Dy systems also have a structure characteristic of REM silicides in direct systems. All this evidences a silicide-like nature of the interaction between surface silicon and the underlying REM film and the formation of the corresponding Gd and Dy silicides on the surface of these systems.

We believe that the totality of the features observed in the photoelectron and Auger spectra can be accounted for by an intense interaction of deposited silicon with a part of surface atoms in the REM film, which occurs during annealing of the Si/REM systems at 450–500°C and leads to the formation of silicide-like bonds between Si and the rare-earth metal. The silicide thus formed, rather than producing a uniform coating, grows in three-dimensional islands on the surface of the starting REM films. This can be due, on the one hand, to the fact that this silicide is a chemically saturated phase and is not bonded to the surface of the REM film. On the other hand, the fairly large lattice mismatch



**Fig. 4.** The Si(2*p*) core-level photoelectron spectra measured for the Si(4 Å)/Gd(0001)/W(110) systems after annealing at 450°C. Shown in the bottom is a Si(2*p*) photoelectron spectrum obtained immediately after deposition of a 20-Å-thick Si layer onto the Gd(0001) surface.

between the silicide and the metal precludes formation of epitaxial silicide phases on the REM surface. The REM silicide islands occupy a small fraction of the surface (they grow apparently primarily near defect clusters in the starting REM films) and, hence, do not affect appreciably the photoelectron spectra and the LEED patterns. As a result, the photoelectron spectra and the LEED patterns generally have a structure and symmetry similar to those observed in the original REM films. The 3D silicide islands become manifest in the valence-band spectra as weak features at binding energies of 1–1.5 and 2–2.5 eV (Fig. 2), as well as in the form of a clearly pronounced silicide-like doublet in the photoelectron spectra of the Si(2*p*) level and a modified Si(LVV) Auger peak in the Auger spectra of the final systems. Experiments involving layer-by-layer Ar-ion etching of the Si/Gd and Si/Dy systems bear out the



**Fig. 5.** Variations in the Auger electron spectra during the deposition of silicon layers with different thicknesses (3, 12, and 50 Å) onto the single-crystal films (a) Gd(0001)/W(110) and (b) Dy(0001)/W(110) measured at room temperature and after annealing at 450–500°C.

above assumptions of the bulk of the REM films remaining unaffected after the interaction with thin Si layers and the accumulation of the reacted silicon on the surface of the REM films. The experiments showed that silicon (in the form of silicide) is distributed directly on the surface of the system, so that etching it off leaves a film of a pure rare-earth metal down to the REM/W(110) interface.

In conclusion, we note that silicide-like bonds between the deposited silicon and an REM start to form already at room temperature. As is seen from Figs. 5a and 5b, the Si(LVV) Auger spectra measured after the deposition of  $\sim 3$  Å Si have a nearly silicide-like struc-

ture. Heating the system to 450–500°C only makes the process more intense, which permits all deposited silicon to react with the rare-earth metal and, thus, to form a thermodynamically stable system.

Thus, the above analysis of the experimental photoelectron spectra [of the valence band and of the Si(2*p*) core level] and the Auger electron spectra of the Si/REM systems studied permits the conclusion that the deposition of thin silicon layers on the surface of the Gd(0001) and Dy(0001) single-crystal films, followed by their annealing at 450–500°C, favors the formation of 3D island films of the silicides of the corresponding REM on the REM surface. After the annealing, the sili-

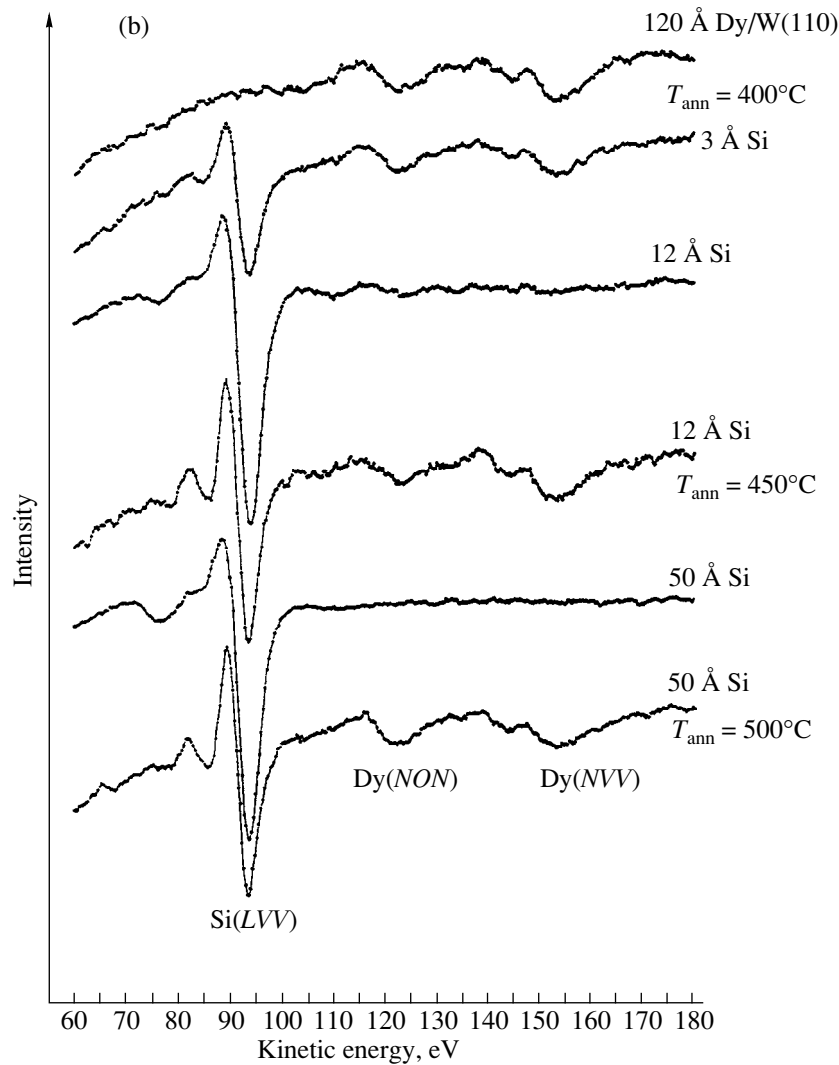


Fig. 5. (Contd.).

side islands occupy a small fraction of the surface. The island-free surface represents the Gd and Dy single-crystal surfaces with a valence-band structure and a symmetry similar to those of the starting REM films.

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