Physics of the Solid State, Vol. 43, No. 2, 2001, pp. 380–385. Translated from Fizika Tverdogo Tela, Vol. 43, No. 2, 2001, pp. 363–368.

LOW-DIMENSIONAL SYSTEMS AND SURFACE PHYSICS

Silicon Interaction with the (0001) Surface of La and Gd Layers

A. Yu. Grigor'ev, O. V. Krupin, D. V. Vyalykh, Yu. S. Dedkov, A. M. Shikin, G. V. Prudnikova, and V. K. Adamchuk

Research Institute of Physics (Petrodvorets Branch), St. Petersburg State University, Ul'yanovskaya ul. 1, Petrodvorets, 198904 Russia

e-mails: shikin@paloma.spbu.ru, adamchuk@paloma.spbu.ru, prudnikg@paloma.spbu.ru

Received June 22, 2000

Abstract—A study is reported on a system consisting of a Si layer on the surface of rare-earth metals (REMs), which is the reverse of a rare-earth metal on silicon, the system of current widespread interest. Interaction of silicon with the (0001) surface of trivalent La and Gd single-crystal layers grown on a W(110) surface is studied by Auger spectroscopy combined with layer-by-layer argon-ion etching of the system and photoelectron spectroscopy. It is found that silicon interacts with the La(0001) and Gd(0001) surfaces even at room temperature with the formation of silicide, but no mutual mixing of the silicon and substrate atoms occurs. When the Si/La(0001) and Si/Gd(0001) systems are heated at 400°C, silicon does not diffuse into the bulk of the metal substrate or to the REM/W(110) interface. © *2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

In recent years, investigations into physicochemical processes in rare-earth-metal–silicon systems have been attracting considerable attention [1]. Interest in these systems is stimulated by their technological potential and the fundamental problems concerning the formation and properties of a metal–semiconductor interface. Most studies of rare-earth-metal–Si systems deal with adsorption of the metal and epitaxial growth of rare-earth metal (REM) silicides on the surface of a single-crystal silicon substrate [1–5]. The increasing interest in layered systems has recently initiated studies dealing with the formation of thin layers of semiconductors, specifically of silicon, on the surface of metals [6, 7]. Earlier [8], we investigated the specific features of the electronic and crystal structures of the systems formed upon deposition of thin silicon layers onto the surface of single-crystal Gd(0001) and Dy(0001) layers, followed by their heating. It was shown that these systems represent essentially single-crystal Gd and Dy layers with Gd and Dy silicide islands lying on the surface of the corresponding metal layers and occupying a small area of the surface of the system.

This paper reports on a study of the systems formed by room-temperature deposition of Si layers, 3 to 50 Å thick, onto the (0001) face of Gd and La single-crystal layers with subsequent heating. The systems were investigated by Auger electron spectroscopy combined with layer-by-layer ion etching and photoelectron spectroscopy. The objects chosen for the study were the Si/Gd(0001) and Si/La(0001) systems, because the first of them has already been investigated and could serve as a reference for the present experiment and the second system could be used for comparing the results obtained on the Si/Gd and Si/Dy structures with systems in which a light trivalent REM is used as a substrate for silicon adsorption. This work was aimed at investigating the processes involved in the interaction of silicon with the (0001) surface of single-crystal La and Gd layers in the course of silicon deposition onto their surfaces and subsequent heating of the systems. We found that the deposited silicon chemically reacts at room temperature with the Gd(0001) and La(0001) surfaces to form the corresponding silicide, with no mutual diffusion of the silicon and metal atoms. As the thickness increases, silicon forms a surface solid layer coating the metal surface and the silicide produced on the interface. When the Si/Gd(0001) and Si/La(0001) systems thus formed are heated at 400°C, silicon does not diffuse into the bulk of La and Gd or to the REM/W(110) interface.

2. EXPERIMENTAL TECHNIQUE

The interaction of silicon with the (0001) surface of La and Gd single-crystal layers grown on the W(110) surface was studied by photoelectron and Auger electron spectroscopy during Si thin-film deposition onto the surface of the metal layers, followed by heating, and in the course of layer-by-layer argon-ion etching of the system thus formed. The photoelectron spectroscopy experiments were carried out on a TGM-3 channel of the BESSY-I synchrotron storage ring (Berlin) with the use of a WSW–ARIES electron analyzer with angular and energy resolution. The total energy resolution of the system was about 150 meV. The photoelectron spectra presented in this work were measured in the

1063-7834/01/4302-0380$21.00

photoelectron takeoff direction normal to the sample surface at an excitation energy of 35 eV, which corresponds approximately to electron emission from the center of the Brillouin zone of La and Gd crystals. Auger electron spectroscopy and layer-by-layer argon-ion etching were performed under laboratory conditions similar to those of the experiments conducted on the BESSY-I. The Auger spectra were recorded with a four-grid retarding-field secondary-electron analyzer at a primary electron energy of 1 keV. The layer-by-layer etching of the samples was carried out by argon ions with a kinetic energy of 1 keV (the angle of incidence on the sample was 60°). The vacuum in both experimental setups was better than 1×10^{-10} torr and deteriorated to 5×10^{-10} torr during the deposition of the metal and silicon films. During the layer-by-layer etching, the argon pressure was 1×10^{-6} torr.

The La and Gd single-crystal layers, about 100 Å thick and with the (0001)-oriented surface, were prepared by the standard technique on the W(110) surface, which provides high crystal perfection and surface cleanness [9]. The metal layers were deposited from a tantalum crucible heated by electron bombardment, and silicon was evaporated from a silicon plate (*n*-Si) heated by direct dc passage.

3. RESULTS

Figure 1 shows the Auger electron spectra of a clean La(0001) surface with 3-, 15-, and 50-Å-thick silicon layers deposited onto it at room temperature and the spectra of a 15-Å-thick Si/La(0001) system formed upon heating at 400°C for 5 min. The lanthanum La(*NOO*), La(*NOV*), and silicon Si(*LVV*) Auger peaks at 59, 78, and 90.5 eV, respectively, are characteristic features of these spectra. Adsorption of a 3-Å-thick Si layer on the La(0001) surface gives rise to the silicon Si(*LVV*) feature in the Auger spectrum of the system. A further increase in silicon concentration on the surface of the system to 15 Å and, subsequently, to 50 Å results in an increase in the intensity of the silicon Auger signal; in the process, the intensity of the signals associated with Auger transitions in the metal decreases gradually, and for a silicon layer 50 Å thick, these signals are not observed in the spectrum. It is readily seen from Fig. 1 that the Auger peaks of both lanthanum and silicon in the Si/La(0001) system vary only weakly in energy in all stages of film formation and lie approximately at the positions that correspond to the pure bulk crystals of the metal and silicon. At the same time, the shape of the Si(*LVV*) Auger peak undergoes changes. This shape is qualitatively characterized by the *A*/*B* ratio of the height of the maximum to the depth of the minimum with respect to the background level, as is shown in Fig. 1. The shape of the peak obtained for the Si layer 50 Å thick coincides with that characteristic of pure crystalline silicon [10]. The shape of the Si(*LVV*) Auger peak for a 3-Å-thick silicon layer differs from that for pure crystalline silicon, which manifests itself

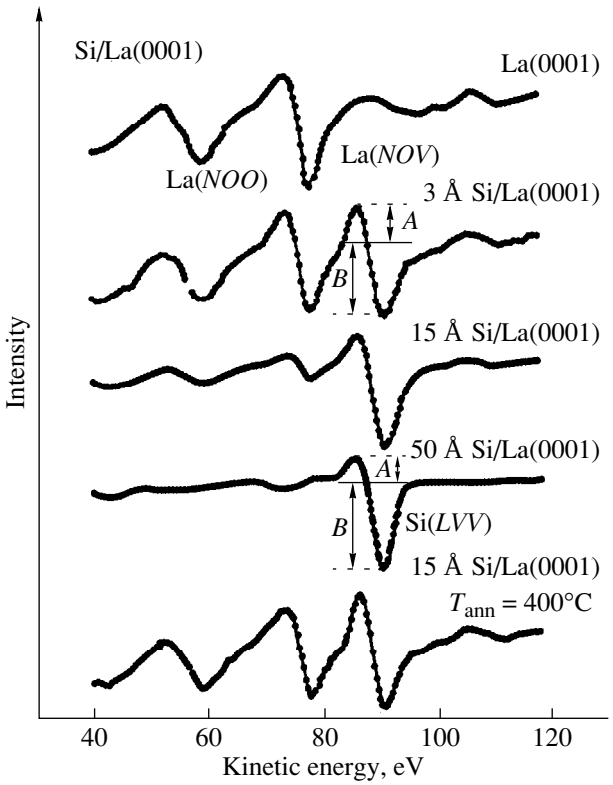

Fig. 1. Evolution of the Auger electron spectra in the course of room-temperature deposition of silicon layers of different thicknesses (3, 15, and 50 Å) onto the surface of an La(0001)/W(110) single-crystal layer and after heating of the system at 400°C.

in an increase in the *A*/*B* ratio. Upon heating the 15-Å-thick Si/La(0001) system at 400°C, the intensity of the lanthanum Auger signals in the spectrum increases to a value close to their initial intensity measured before silicon deposition on the metal surface. The shape of the silicon Auger peak varies substantially, and the *A*/*B* ratio for the system formed as a result of the heating is increased compared to that for pure silicon.

The Auger spectra of the Si/Gd(0001) system (Fig. 2) change in the same way as those of Si/La(0001). Figure 2 shows the Auger spectra for a clean Gd(0001) surface, silicon layers (3, 12, and 50 Å thick) deposited onto the Gd(0001) surface at room temperature, and a 12-Å-thick Si/Gd(0001) system heated at 400°C. The Si/Gd(0001) system is characterized by gadolinium Auger peaks at kinetic energies of 111 eV [Gd(*NOV*)] and 141 eV [Gd(*NVV*)] and by a silicon Si(*LVV*) Auger peak at 92 eV. Similar to the Si/La(0001) system, deposition of silicon onto the Si/Gd(0001) surface results in an increase in the intensity of the silicon Auger signal and a gradual decrease in the intensity of the metal Auger signals. Adsorption of a thick Si layer leads to the formation of a system whose Auger spectrum is similar to that of pure silicon. Heating the 12-Å-thick Si/Gd(0001) system at 400°C brings about an increase

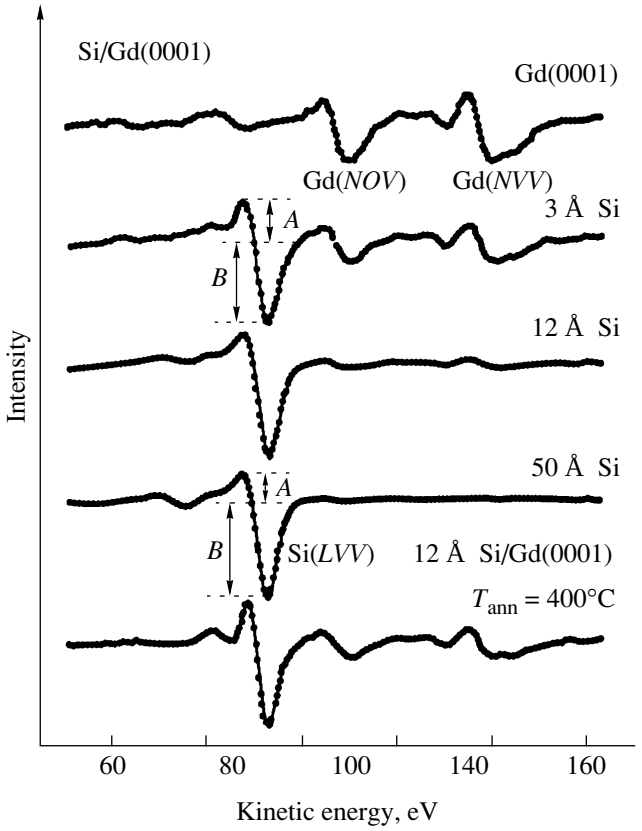

Fig. 2. Evolution of the Auger electron spectra in the course of room-temperature deposition of silicon layers of different thicknesses (3, 12, and 50 Å) onto the surface of a Gd(0001)/W(110) single-crystal layer and after heating of the system at 400°C.

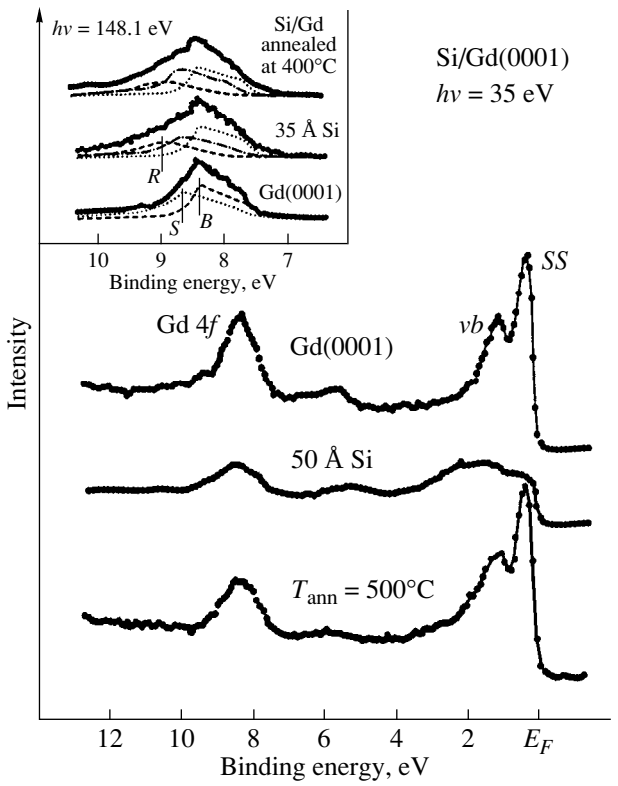

Fig. 3. Photoelectron spectra of the Gd valence band and Gd 4*f* electrons for a clean Gd(0001)/W(110) layer and a 50-Å-thick Si/Gd(0001)/W(110) system formed at room temperature and after heating at 500°C. The inset shows photoemission spectra of the Gd 4*f* electrons at the photoexcitation energy $h\nu$ = 148.1 eV, which corresponds to the resonant excitation energy of the 4*d*–4*f* transition in the metal, for a clean Gd(0001) surface, and a 35-Å-thick Si/Gd(0001) system produced at room temperature and after heating at 400°C.

in the intensity of the Gd Auger signals and a change in the shape of the silicon Auger peak. As in the case of Si/La(0001), the shape of the Si(*LVV*) Auger peak, which differs from that of bulk silicon, is also observed for the system formed upon the adsorption of a thin Si layer 3 Å thick on the Gd(0001) surface at room temperature.

Figure 3 displays the photoemission spectra recorded at a normal photoelectron takeoff from the sample surface for a clean Gd(0001) surface, after deposition of a 50-Å-thick Si layer onto the surface of the metal, and for a 50-Å-thick Si/Gd(0001) system heated at 500°C for 5 min. The spectrum of the clean Gd(0001) surface is characterized by peaks corresponding to photoemission from surface states near the Fermi level, *d* states of the valence band at a binding energy of approximately 1.2 eV, and 4*f* states of the metal at 8.3 eV. The emission near 6 eV is due to a slight oxygen impurity present on the metal surface. As is seen from Fig. 3, after the deposition of the Si layer 50 Å thick onto the Gd(0001) surface, the features corresponding to the surface states and the Gd valence band practically disappear in the spectrum of the system and the 4*f* signal of the metal decreases substantially in intensity (by approximately a factor of four). At the same time, a new broad feature is observed at a binding energy of approximately 2 eV. Heating of the system thus formed at 500°C restores the spectral features characteristic of a clean Gd(0001) surface. In this case, the 4*f* electron photoemission intensity increases to a value close to that of the Gd 4*f* electrons from a clean Gd(0001) surface. As a result, after the heating, the photoemission spectrum of the 50-Å-thick Si/Gd(0001) system becomes similar to that of the clean Gd(0001) surface before silicon deposition.

The inset to Fig. 3 shows the photoemission spectra of the region of the Gd 4*f* electronic states which were recorded at a resonant excitation energy of 148.1 eV. The spectra are shown for a clean Gd(0001) surface, a 35-Å-thick Si layer deposited onto the Gd(0001) surface at room temperature, and a 35-Å-thick Si/Gd(0001) system subjected to heating at 400°C. Analysis of the results obtained revealed that the spectra contain several components corresponding to the emission of 4*f*

electrons of different groups of atoms. The spectrum of a clean Gd(0001) surface consists of the component *B* due to photoemission from atoms in the bulk and the photoemission component *S* originating from atoms localized on the Gd surface. As is seen from the figure, adsorption of a 35-Å-thick Si layer reduces the intensity of the surface component *S* as compared to the total intensity of emission from the 4*f* states and results in the appearance of a new 4*f* emission component *R*. Heating the system brings about an increase in the intensity of the surface component and a decrease in that of the new component.

4. DISCUSSION

As follows from an analysis of Figs. 1 and 2, deposition of a thin Si layer 3 Å thick onto the La(0001) and Gd(0001) surfaces at room temperature results in the appearance of a Si(*LVV*) Auger peak in the spectra of the systems and its shape differs from that in the Auger spectrum of pure single-crystal silicon [10]. Because the Si(*LVV*) Auger peak is an indication of the chemical state of the Si atoms, the difference between its shape and the shape of the peaks characteristic of pure bulk silicon suggests a change in the chemical state of the silicon atoms in these systems compared to that in bulk silicon. This implies that, at room temperature, silicon chemically interacts with REM atoms on the La(0001) and Gd(0001) surfaces. This is supported by the appearance of a new reactive component *R* in the Gd 4*f* photoemission spectrum of the system formed by room-temperature deposition of a silicon layer 35 Å thick on the Gd(0001) surface (see inset in Fig. 3).

Further deposition of silicon results in a weakening of the metal substrate signals in the Auger spectra of the Si/La and Si/Gd systems, and they disappear completely at a silicon layer thickness of 50 Å. The features associated with the valence band and the surface state of the metal overlap with a new broad feature in the photoemission spectrum of the system (Fig. 3). According to studies on the electronic states of the Si valence band, this feature observed in the photoemission spectrum of the 50-Å-thick Si/Gd(0001) system can be assigned to the formation of sp^3 hybridized bonds between silicon atoms [11]. Therefore, it can be concluded that deposition of a sufficiently thick silicon layer (50 Å) onto an REM surface at room temperature brings about the formation of a continuous layer of silicon with the properties of bulk Si, which covers the metal surface and the silicide layer formed at the interface.

The formation of a continuous silicon layer on the surface of the system produced by room-temperature deposition of a 50-Å-thick silicon layer onto the La(0001) and Gd(0001) surfaces allows us to conclude that, at room temperature, atoms from the deposited silicon layer and from the metal substrate do not undergo mutual diffusion to the extent which would involve a considerable part of the deposited silicon. It can be assumed that the high stability of the La(0001) and Gd(0001) single-crystal surfaces or of the silicide layer formed on these surfaces at room temperature creates a barrier to mutual diffusion of the silicon and metal atoms. The question naturally arises as to whether such a barrier can be overcome, for instance, by heating the system to a high temperature at which mutual diffusion of the silicon and metal atoms would take place.

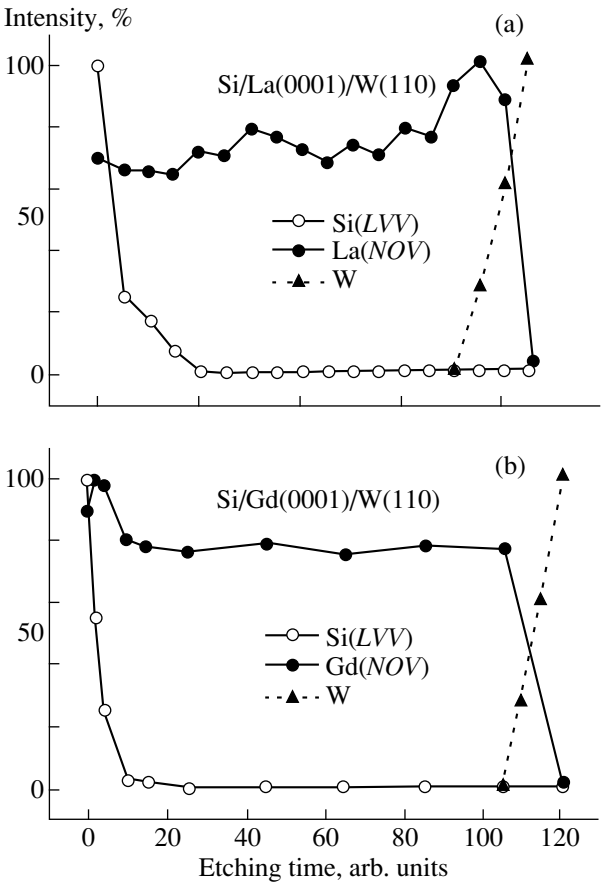

Fig. 4. Relative variation of the Si($L_{23}VV$), La($N_{45}O_{23}V_{67}$), and Gd($N_{45}O_{23}V_{67}$) Auger peak amplitudes in the course of layer-by-layer etching of (a) 15-Å Si/La(0001)/W(110) and (b) 12-Å Si/Gd(0001)/W(110) systems preliminarily heated at 400°C.

As can be seen from the Auger spectra of the 15-Å Si/La(0001) and 12-Å Si/Gd(0001) systems heated at 400°C, the heating results in an increase in the intensity of the Auger signals of the metals as compared to silicon (Figs. 1, 2). The shape of the Si(*LVV*) Auger peak also changes and becomes similar to that observed in the case of the epitaxial REM silicides on the surface of single-crystal silicon [10]. The fact that the energy location of the Auger peaks virtually does not change for the system after the heating, as compared to a clean metal surface and a bulk silicon layer, suggests a covalent nature of the chemical interaction with a weak

charge transfer between the atoms, which is characteristic of chemical bonding in REM silicides. The heating of even a thick (50 Å) Si layer deposited onto the Gd(0001) surface at room temperature produces a system whose valence-band photoemission spectrum is similar to that of a clean Gd(0001) surface, even though the presence of silicon on the surface becomes manifest in the observation of a reactive component in the 4*f* electron photoemission of the metal (see inset in Fig. 3). This means that the system consists of considerable areas of clean metal surface and regions coated by metal silicide occupying a smaller part of the surface area of the system. This is supported by the fact that the silicide does not provide a noticeable contribution to the valence-band photoemission spectra of the heated system. If we assume that upon heating, silicon atoms form silicide which builds up on the surface in the form of islands, it becomes difficult to understand why the silicide formed from a silicon layer 50 Å thick weakly manifests itself in the valence-band photoemission spectra of the system. It can be assumed that the major part of silicon leaves the surface in the course of heating. One possible explanation for this effect could be the diffusion of silicon into the bulk of the metal substrate or to the REM/W(110) interface.

In order to establish whether Si atoms diffuse under heating of the system into the bulk of the metal or to the REM/W(110) interface, the heated 12-Å Si/Gd(0001) and 15-Å Si/La(0001) systems were subjected to layer-by-layer etching with Ar^+ ions. The etching of each layer was followed by the recording of Auger electron spectra. Analysis of the results obtained revealed dependences of the intensities of the Si(*LVV*), La(*NOV*), and Gd(*NOV*) Auger signals on the depth of the removed layer, which are displayed in Figs. 4a and 4b for the Si/La(0001) and Si/Gd(0001) systems, respectively. These dependences reproduce the depth profiles of the silicon and metal concentrations in the system. We readily see that the intensity of the silicon Auger signal and, hence, the silicon atom concentration on the surface of the system decrease with an increase in the thickness of the removed layer. As the depth of etching increases, the silicon concentration in both the Si/La and Si/Gd systems decreases almost to zero and the silicon Auger signal does not appear until the etching is terminated; in this case, the Auger spectra contain only the signal due to the tungsten substrate. The intensities of the La and Gd Auger signals undergo changes at the beginning and the end of the etching, i.e., at the Si/REM and REM/W(110) interfaces, which is accounted for by the effect of the interface structure. On the whole, the Auger signal intensity of the metal in the system varies only weakly with the depth of the removed layer and decreases to zero at the end of the etching, when the Auger signal due to the tungsten substrate appears.

The depth profiles of the Si and metal atoms in the Si/La(0001) and Si/Gd(0001) systems indicate that Si is present only on the surface of the systems and not in the bulk of the metal or at the REM/W(110) interface. Therefore, we can conclude that heating of the Si/La(0001) and Si/Gd(0001) systems does not give rise to diffusion of silicon atoms into the bulk of the metal substrate or to the tungsten substrate interface. This suggests that, upon heating of the Si/La(0001) and Si/Gd(0001) systems, silicon and silicide formed at the interface between the deposited silicon layer and the metal substrate diffuse over the surface of the single-crystal metal layer and build up on surface defects, such as breaks in the metal layer, or at the sample boundary, which may become a subject of further study of the Si/REM system.

5. CONCLUSION

The present study of the Si/La(0001) and Si/Gd(0001) systems by photoemission and Auger electron spectroscopy combined with layer-by-layer Ar^+ ion etching allowed us to conclude that deposition of a silicon layer onto Gd(0001) and La(0001) surfaces at room temperature activates the formation of silicide at the Si/REM interface; however, no mutual diffusion of silicon and metal atoms occurs. Further deposition of silicon brings about the formation of a continuous silicon layer on the surface of the system. When the Si/La(0001) and Si/Gd(0001) systems are heated at 400°C, silicon atoms do not diffuse into the bulk of the substrate or to the REM/W(110) interface. It was conjectured that silicon and silicide formed at the Si/REM interface at room temperature diffuse under heating over the (0001) surface of the single-crystal metal and build up on surface defects and at the sample boundary.

ACKNOWLEDGMENTS

The authors are grateful to the administration and personnel of the BESSY I Synchrotron Radiation Center (Berlin, Germany) for the opportunity to perform photoemission experiments on a synchrotron beam. The authors thank Prof. G. Kaindl and O. Weschke of the Free University (Berlin) for providing the research equipment on which to carry out the photoemission experiments and for their useful discussions of the results.

This work was supported by the "Surface Atomic Structures" Program (project no. 2.1.99) and the Russian Foundation for Basic Research (project no. 96-02-00045G).

REFERENCES

1. Falko P. Netzer, J. Phys.: Condens. Matter **7**, 1023 (1995).
2. L. Braicovich, *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Ed. by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1988), Vol. 5.

3. R. Anderson, J. E. Baglin, J. J. Dempsey, *et al.*, Appl. Phys. Lett. **35**, 285 (1979).
4. K. N. Tu, R. D. Thompson, and B. Y. Tsaur, Appl. Phys. Lett. **38**, 626 (1981).
5. H. Norde, Pires J. de Sousa, F. M. Heurle, *et al.*, Appl. Phys. Lett. **38**, 626 (1981).
6. J. A. Martín-Gago, C. Rojas, C. Polop, *et al.*, Phys. Rev. B **59**, 3070 (1999).
7. T. Suzuki and Y. Gotoh, Thin Solid Films **330**, 125 (1998).
8. A. M. Shikin, A. Yu. Grigor'ev, G. V. Prudnikova, *et al.*, Fiz. Tverd. Tela (St. Petersburg) **42**, 942 (2000) [Phys. Solid State **42**, 973 (2000)].
9. C. Schüßler-Langeheine, R. Meier, H. Ott, *et al.*, Phys. Rev. B **60**, 3449 (1999).
10. M. Sancrotti, A. Iandelli, G. L. Olcese, and A. Palenzona, Phys. Rev. B **44**, 3328 (1991).
11. G. Le Lay, M. Göthelid, T. M. Grehk, *et al.*, Phys. Rev. B **50**, 14277 (1994).

Translated by G. Skrebtsov