Flatband Conditions Observed for Lanthanide-Silicide Monolayers on *n*-Type Si(111)

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We report on a core-level photoemission study of lanthanide silicides epitaxially grown on *n*-type Si(111). In the monolayer regime, an extremely low band bending is observed for the first time, with a Fermi-level position only 0.08 ± 0.05 eV below the conduction-band minimum of silicon. With increasing coverage, the Fermi-level position moves towards a final Schottky-barrier height of 0.32 ± 0.05 eV. This behavior is assigned to the developing metallicity of the silicide overlayer. [S0031-9007(99)08594-4]

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The interaction of metal overlayers with semiconductor surfaces is a matter of broad interest because of its importance for contacts in large-scale integration. From the technological point of view, a main goal is to find materials yielding a low Schottky-barrier height as well as forming a stable interface with low lattice mismatch. Until now, only a few Schottky contacts to *n*-type Si are known with a barrier height below one half of the Si band gap [1,2]. Silicides of the heavy trivalent lanthanides (Ln) on Si(111) show barrier heights of only 0.3–0.4 eV, currently representing the lowest known values for metal/*n*-Si contacts [3]. Moreover, their small lattice mismatch to the Si(111) substrate leads to epitaxial growth with a high degree of structural perfection [3–6]. These interfaces are thus an ideal system both for a microscopic understanding of the mechanisms of Schottky-barrier formation and for applications as Ohmic contacts. Furthermore, their correspondingly large barrier height on *p*-type Si [7] is an interesting property for infrared detectors or photovoltaic applications.

In this Letter, we report on a detailed study of the Schottky-barrier formation and the chemical composition of different epitaxially grown Ln silicides on *n*-type Si(111) by means of high-resolution core-level photoemission spectroscopy. In the monolayer regime, we found the lowest barrier heights ever observed for metal/*n*-Si interfaces, increasing towards higher values with growing film thickness. This behavior will be discussed in the framework of theoretical models for Schottky-barrier formation.

The photoemission experiments were performed at the PM-2 and PM-5 beam lines of the Berlin storage ring BESSY I, using a hemispherical Leybold EA-11 electron-energy analyzer in normal-emission geometry. The total-system resolution varied between 200 and 300 meV (FWHM), depending on the photon energy. In addition, scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) were used for structural analysis. Clean, well-ordered substrate surfaces were prepared by annealing *n*-type Si(111) wafers (10–20 Ω cm) at 1100 °C and subsequent slow cooling down [8]. The silicide films were grown by vapor-phase deposition of different high-purity Ln metals (Gd, Dy, Er, and Lu) out of W crucibles heated by electron bombardment. The evaporation rates of typically 1 Å/min were controlled using a quartz-crystal thickness monitor. Subsequent annealing at 500–600 °C yields epitaxially ordered silicide films.

A variety of techniques has been used to determine the atomic structure of epitaxial Ln silicides on Si(111), with the main emphasis on Dy and Er silicides [9–12], which behave in a similar way. It can be assumed that these findings are representative for all members of the chemically similar heavy trivalent Ln. For silicide coverages of one monolayer, prepared from about 2.6 Å Ln, a $p(1 \times 1)$ structure is formed, consisting of an ordered hexagonal monolayer of Ln atoms accommodated underneath a buckled Si surface layer, as shown in Fig. 1a. This structure can be considered a single $\mathrm{LnSi_2}$ layer [9]. With increasing coverage, the growth of epitaxially ordered $\mathrm{Ln_3Si_5}$ layers is observed, as depicted in Fig. 1b. These bulklike silicides form a defected $\mathrm{AlB_2}$-type structure, consisting of stacked hexagonal Ln planes and graphitelike Si planes with an ordered arrangement of Si vacancies. Its surface is again formed by a buckled Si layer without vacancies and was shown to be essentially identical to that of the monolayer silicide [10,11]. In LEED experiments, the characteristic $\sqrt{3} \times \sqrt{3}\ R30°$ pattern is observed, which is assigned to an ordered superlattice of Si vacancies. It should be mentioned that the growth of thick layers is accompanied by pinholes, stacking faults, and screw dislocations, as demonstrated in STM images like the one in Fig. 1c.

In Fig. 2, a representative set of Si-2p spectra as a function of Er exposure is shown, together with the components of a least-squares fit analysis. Very similar spectra were observed for the other Ln silicides investigated in this study. The data are taken at different photon energies in order to tune the surface sensitivity. The spectra are well described by a superposition of Lorentzian peaks (FWHM = 0.08 ± 0.02 eV) convoluted by a Gaussian for describing both experimental resolution and crystalline order. An exponential background was used to simulate the secondary-electron contribution at $h\nu = 110$ eV, and an integral background was taken at $h\nu = 130$ eV.

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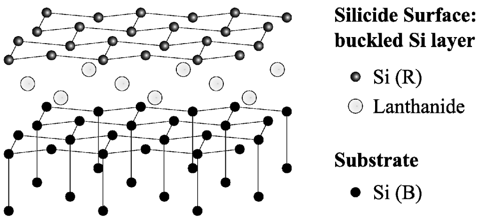
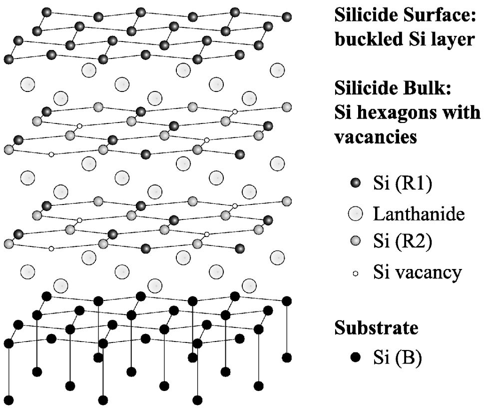
(a) 1 monolayer $LnSi_2/Si(111)$



(b) 3 monolayers $Ln_3Si_5/Si(111)$



(c) 8 monolayers $Ln_3Si_5/Si(111)$

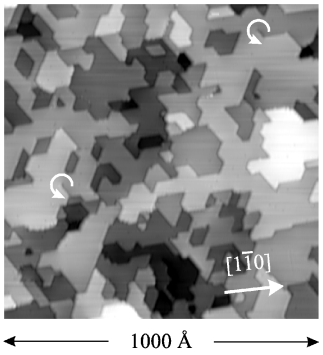


FIG. 1. Atomic structure of (a) 1 monolayer $LnSi_2$ and (b) 3 monolayers Ln_3Si_5 on Si(111). (c) STM image of 20 Å Dy deposited on Si(111) and annealed subsequently at 600 °C. Some screw dislocations are indicated by arrows.

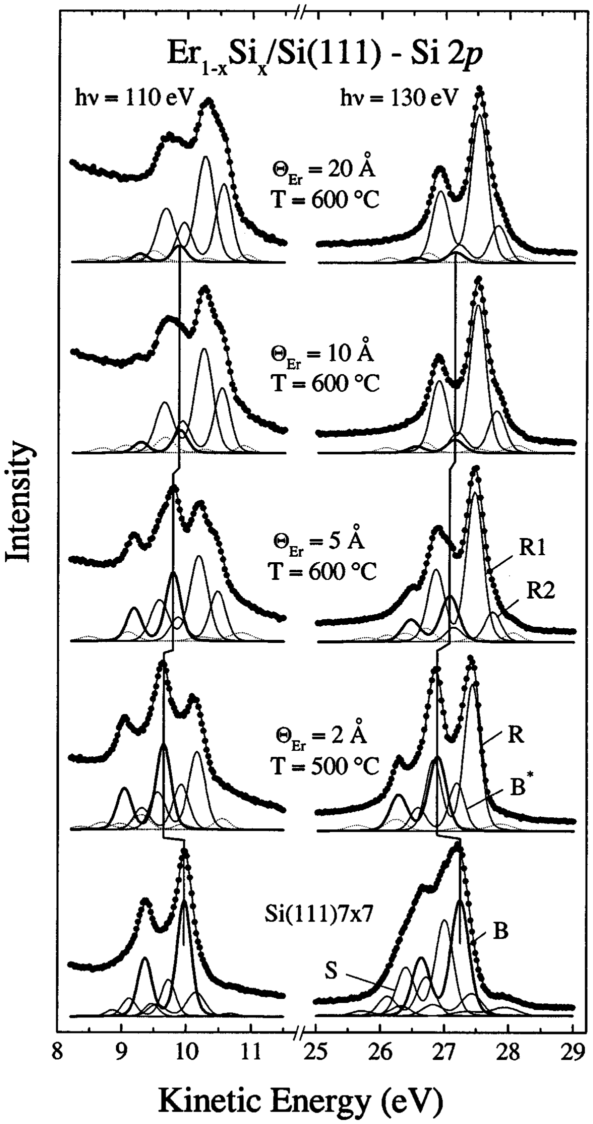


FIG. 2. Photoemission spectra of the Si-2p core level taken at $h\nu = 110$ and 130 eV as a function of Er coverage. The spectra (solid dots), normalized to equal heights, are shown together with the corresponding line-shape analysis, consisting of substrate bulk (*B*, thick lines), substrate surface (*S*, thin lines), reacted silicides (*R*, *R*1, *R*2: thin lines) and minor components related to edges, pinholes, and screw dislocations (dotted lines). The band-bending behavior is indicated by the thick vertical lines.

The spectra of the bare Si(111)-(7 × 7) surface consist of five identically spin-orbit split doublets, which originate from the substrate bulk (thick subspectrum *B*) and different surface sites (thin subspectra *S*) [13]. At Er coverages of 2 Å, the substrate-bulk signal shifts to lower kinetic energies. This observation is caused by band bending and will be discussed in detail further below. In addition, the Si-2p substrate emission is now superposed by one doublet from the $ErSi_2$ silicide monolayer (thin subspectrum *R*), shifted by 0.54 ± 0.03 eV to higher kinetic energies with respect to the bulk-substrate component. This chemical shift is assigned to a charge transfer from Er to Si, the latter one being the element with higher electronegativity. Furthermore, there is still a weak unshifted spectral contribution (B^*) from the initial bare Si(111)-(7 × 7) surface, demonstrating that the surface is not completely covered by the silicide monolayer. This behavior is also supported by STM images (not shown here).

Upon growth of 5 Å Er and more, i.e., for several monolayer thick films, the substrate component shifts back to higher kinetic energies. The emission from the Er_3Si_5 overlayer is now characterized by two silicide doublets (thin subspectra *R*1 and *R*2) shifted by 0.36 ± 0.04 eV and 0.65 ± 0.04 eV to higher kinetic energies with respect to the bulk-substrate component.

With increasing coverage, the substrate component decreases in relative intensity, while the silicide emission becomes dominant. Therefore bulk sensitive measurements at $h\nu = 110$ eV and $h\nu = 250$ eV were performed for monitoring the development of band bending with silicide thickness. Nevertheless, the Si-2p spectra at 10 and 20 Å Er are very similar, as observed in Fig. 2. The most striking difference is the decreasing shoulder at kinetic energies around 9.8 eV for the spectra taken at $h\nu = 110$ eV. This difference is considered a fingerprint of the substrate emission, which is expected to contribute more to the spectrum at 10 Å. In this way, the substrate core level is found to shift back to higher kinetic energies with increasing coverage.

In general, the Ln-silicide components are characterized by very sharp core-level features, indicating a high crystallinity. Furthermore, there are weak spectral contributions (dotted subspectra) at the low- and high-energy sides of the Si-2p emission, which regularly amount to less than 5% of the total spectral intensity. These subspectra are attributed to particular atomic sites at terrace edges, pinholes, or screw dislocations, as observed in Fig. 1c.

The two different spectral components $R1$ and $R2$, which were observed for thick $\mathrm{Ln_3Si_5}$ films, but not in case of the $\mathrm{LnSi_2}$ monolayers, can be assigned to lattice sites within a simple model. The layered crystallographic structure of the epitaxial Ln silicide evokes a strong bonding anisotropy, resulting in the formation of Si sp^2 hybrids. This in-plane bonding is assumed to play the major role for the Si-2p core-level shifts, while surface effects are less important. As shown in Fig. 1b, there are two inequivalent sites of silicon atoms in the hexagonal planes of $\mathrm{Ln_3Si_5}$: those bound to three next silicon atoms and those located next to a silicon vacancy, bound only to two silicon atoms. Hence two spectral components $R1$ and $R2$ are expected. This view is in good agreement with the observation of only one silicide component R in the monolayer regime, where one single bonding configuration exists for the Si atoms in the silicide, as shown in Fig. 1a.

Via the relative photoemission intensities of the spectral components $R1$ and $R2$ at different photon energies and coverages, component $R1$ can be related to silicon atoms bound to three silicon atoms and $R2$ to silicon atoms with neighboring vacancies, the latter contributing more at higher bulk sensitivity. This assignment is further supported by the observed magnitude of the chemical shifts of $R1$ and $R2$, which reflect theoretical predictions of a larger charge transfer from Ln atoms to the silicon atoms labeled $R2$ than to those labeled $R1$ [14].

The variations of the Schottky-barrier height with film thickness of the four different Ln silicides investigated in this study are presented in Fig. 3. All four systems show barrier-height variations quite close to each other, reflecting the remarkable similarity of the heavy trivalent Ln metals.

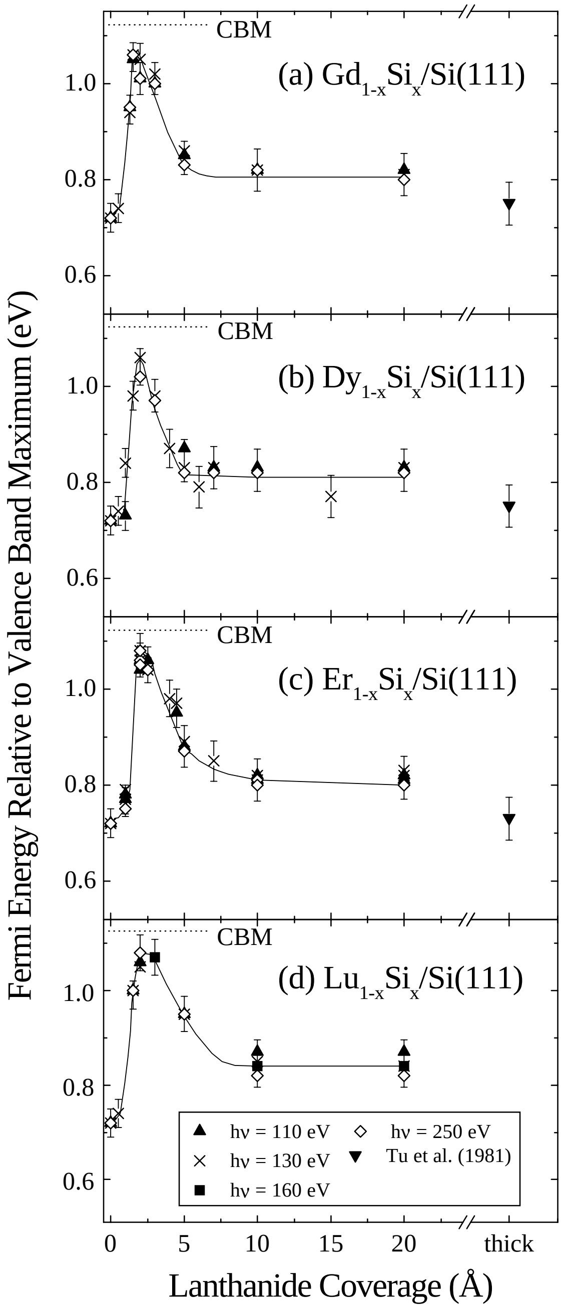


FIG. 3. Development of the Fermi-level position in the band gap of silicon for silicides of Gd, Dy, Er, and Lu as a function of Ln coverage.

The main issue of this Letter concerns the initial band-bending induced shifts of the core-level line from the substrate bulk. Whereas only minute variations are observed in the submonolayer range, the substrate component shifts by about 0.32 ± 0.04 eV to lower kinetic energies at 2 Å coverage, as compared with Si(111)-(7 × 7). With the initial Fermi-level position of pristine Si(111)-(7 × 7) located at 0.72 ± 0.03 eV above the valence-band maximum (VBM) [15], the resulting position of the Fermi level for one monolayer amounts to only 0.08 ± 0.05 eV below the conduction-band minimum (CBM), representing flatband conditions and therewith the lowest band bending ever observed for metal/n-Si interfaces. At higher coverages, the Schottky-barrier height increases towards a value of 0.32 ± 0.05 eV, which is in nice agreement with literature data from current-voltage measurements amounting to 0.37 ± 0.03 eV [3].

At present, only a first attempt can be made to understand the observed band-bending behavior and especially the remarkable overshoot in the monolayer range. Similar overshoots have been observed frequently for metal overlayers on semiconductor substrates in the low-coverage regime [16]. It is widely accepted that the Schottky-barrier formation is mainly determined by the properties of metal-induced gap states (MIGS), being electronic states from the metal coupling to semiconductor states with complex wave vector energetically located in the band gap [17–19]. The charge transfer mediated by the MIGS results in an interface dipole and therewith in a discontinuity of the vacuum energy at the interface. The MIGS lead to a Fermi-level position close to its charge-neutrality level, which is usually located in the midgap region [1,17,18]. The specific interface structure was found, however, to play an additional role because of its strong influence on the charge-neutrality level of the MIGS and therewith on the interface dipole [2,20,21]. In principle, the coverage-dependent structure of the silicide layer may lead to the observed overshoot. On the other hand, flatband conditions have not been observed for any metal-silicon interface up to now, so that a further mechanism is expected to contribute.

In the present case, the final Fermi-level position can be explained by the MIGS model. It is obtained for coverages above 3 monolayers of Ln_3Si_5, where the overlayer has assumed the full metallic character of the bulk silicide with a low resistivity [22] and a high density of states around the Fermi level [23–25]. For the $ErSi_2$ monolayer, in contrast, a rather low density of states is observed at the Fermi level [25]. Its electronic structure is characterized by a Fermi surface consisting of small electron and hole pockets typical for a semimetal [26]. Thus it can be assumed that there is a too low density of overlayer states and therewith of MIGS for providing a sufficient charge transfer, resulting in a negligible interface dipole. In this case, band bending is rather determined by the classical work-function model characterized by a continuous vacuum level [27]. With the work function of the silicide being below that of silicon, a Fermi-level position close to the CBM is reasonable.

It should be noted that this preliminary discussion is mainly intended to stimulate progress in this rather complex topic. For a better understanding of the overshoot behavior, detailed theoretical studies of this system are necessary.

In summary, the Schottky-barrier formation and the chemical composition of various epitaxially grown Ln silicides on n-type Si(111) were investigated by means of high-resolution core-level photoemission. The Schottky-barrier height was found to vary strongly with the film thickness of the silicide, showing flatband conditions in the monolayer regime. This observation was assigned to the reduced metallicity of the silicide monolayer.

In order to exploit our results for device applications, a method has to be developed to conserve the extreme electronic properties of the silicide monolayer. The overgrowth, e.g., by epitaxial silicon layers, which can even be extended to multilayer formation, will be a challenging research field in the future.

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[1] W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer-Verlag, Berlin, 1995).
[2] W. Tung, J. Vac. Sci. Technol. B **11**, 1546 (1993).
[3] K. N. Tu, R. D. Thompson, and B. Y. Tsaur, Appl. Phys. Lett. **38**, 626 (1981).
[4] J. A. Knapp and S. T. Picraux, Appl. Phys. Lett. **48**, 466 (1986).
[5] R. D. Thompson, B. Y. Tsaur, and K. N. Tu, Appl. Phys. Lett. **38**, 535 (1981).
[6] R. Baptist *et al.*, Phys. Rev. Lett. **64**, 311 (1990).
[7] H. Norde *et al.*, Appl. Phys. Lett. **38**, 865 (1981).
[8] I. Manke *et al.*, J. Vac. Sci. Technol. B **13**, 1657 (1995).
[9] P. Wetzel *et al.*, Phys. Rev. B **47**, 3677 (1993).
[10] P. Wetzel *et al.*, Surf. Sci. **355**, 13 (1996).
[11] T. P. Roge *et al.*, Phys. Rev. B **51**, 10 998 (1995).
[12] S. Vandré *et al.*, Appl. Surf. Sci. **123/124**, 100 (1998).
[13] C. J. Karlsson *et al.*, Phys. Rev. B **50**, 5767 (1994).
[14] G. Allan, I. Lefebvre, and N. E. Christensen, Phys. Rev. B **48**, 8572 (1993).
[15] M. T. Cuberes *et al.*, J. Vac. Sci. Technol. B **12**, 2422 (1994).
[16] W. Mönch, Appl. Surf. Sci. **41**, 128 (1989).
[17] J. Tersoff, Phys. Rev. Lett. **52**, 465 (1984).
[18] F. Flores and C. Tejedor, J. Phys. C **20**, 145 (1987).
[19] F. Bechstedt and M. Scheffler, Surf. Sci. Rep. **18**, 145 (1993).
[20] R. G. Dandrea and C. B. Duke, J. Vac. Sci. Technol. B **11**, 1553 (1993).
[21] J. P. Sullivan *et al.*, J. Vac. Sci. Technol. B **11**, 1564 (1993).
[22] J. Y. Duboz *et al.*, Appl. Phys. Lett. **55**, 84 (1989).
[23] L. Stauffer *et al.*, Phys. Rev. B **46**, 13 201 (1992).
[24] T. Rössler and C. Laubschat (private communication).
[25] S. Vandré *et al.*, J. Vac. Sci. Technol. B (to be published).
[26] P. Wetzel *et al.*, Solid State Commun. **82**, 235 (1992); L. Stauffer *et al.*, Phys. Rev. B **47**, 10 555 (1993).
[27] W. Schottky, Naturwissenschaften **26**, 843 (1938).