Photoemission study of the initial stage of Er/Si(100) interface formation

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Abstract

The initial stage of Er/Si(100) interface formation has been investigated by using synchrotron radiation photoelectron spectroscopy combined with low-energy electron diffraction. Both the valence band and the core level peaks of the Si photoemission spectra shift rigidly with increasing Er coverage in the submonolayer region. Upon depositing 0.6 monolayers of Er on the Si(100) surface at room temperature, the surface Fermi level is ultimately pinned at 0.29 eV above its initial value, which is equivalent to a Schottky barrier height of 0.67 eV. No evidence is found for the formation of Er silicides at the as-deposited surfaces. Annealing of the Er-covered Si(100) surfaces at 600 °C results in the appearance of a new peak located 1.2 eV below the Si 2p peak, indicating the presence of some sort of Er silicide. Meanwhile, the Er 4f spectrum measured for samples upon annealing exhibits a well-resolved fine structure, implying that only monospecies of Er silicide may exist on the surface.

The behaviour of Er/Si interfaces and the process of formation of Er silicides on Si surfaces have recently attracted great interest, from both technological and fundamental viewpoints. The very low Schottky barrier heights (SBHs) of Er and Er silicide on n-type Si and the lowest resistance of Er silicide of all the rare-earth metal silicides [1, 2] make this system one of the most promising materials for contacts in large-scale integration [3]. Er silicides can be grown epitaxially on an Si(111) substrate with minor lattice mismatch, while large anisotropic lattice mismatch of Er silicides on Si(100) makes the growth of artificial low-dimensional structures possible [4]. The photoemission of Er/Si(111) and Er silicide/Si(111) interfaces has been the subject of many recent investigations [5–10]. It was observed that interfacial reactions could occur in such systems even at room temperature (RT). However, studies of the Er/Si(100) interface are relatively rare [11, 12], even though (100) is the most important

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surface of silicon in device technology. For the Er/Si(100) system the questions of whether the interfacial reaction also occurs at RT, how the Schottky barrier forms and what is the effect of annealing on the RT deposited ultra-thin films are still open. In this work, the early stage of Er/Si interface formation on Si(100) is studied using photoelectron spectroscopy excited by synchrotron radiation (SRPES). The Si 2p core level spectra, the Er 4f valence band spectra and the work function (WF) are carefully measured during the whole process. The relatively high energy resolution possessed by SRPES enables us to observe subtle variations of the spectra and hence to give a detailed description of interface formation. It is found that the RT deposition of Er onto a p-type Si(100) substrate results in prompt pinning of the surface Fermi level without interfacial reaction, whereas the moderate annealing of Er-covered Si(100) surfaces gives rise to the formation of monospecies of Er silicide.

The experiments were carried out on beamline SGM1 of ISA at the Institute for the Storage Ring Facilities of the University of Aarhus in Denmark. The beamline consists of a spherical grating monochromator with a Scienta-type hemispherical analyser which ensured an overall energy resolution of $\sim$0.1 eV for the photon energy range of 20–200 eV adopted in the present study. The experimental system comprises a sample preparation chamber equipped with a low-energy electron diffraction (LEED) facility and a SCIENTA surface analysis chamber equipped with a photoelectron spectrometer. The base pressure of each chamber was less than 3×10^{-8} Pa. The photoemission spectra were taken under angle-integrated conditions with the incident angle and axial emission angle kept at $45°$ and $0°$ respectively.

A p-Si(100) wafer with a resistivity of 1–5 Ω cm was used as the substrate. It was chemically cleaned by rinsing in hydrofluoric acid and deionized water. Vacuum cleaning of the sample surface was carried out in the preparation chamber by heating to $1100\,°C$. An atomically clean Si(100) surface with a (2×1) reconstruction was observed by LEED. Er atoms were then evaporated from an Er rod heated by electron bombardment. The thickness of the Er layer was estimated by comparing the measured WF values with those available in the literature [12]. It should be mentioned that above the coverage of 1.5 monolayers (ML), the thickness control method used here is rather a rough one, since the referenced WF data were measured at a relatively low temperature (230 K). In the submonolayer region of interest here, the temperature difference would not have a significant influence, according to [12]. The WF of our sample was determined by the whole valence spectrum taken at an incident photon energy of 26 eV. The amount of Er deposited was increased step by step with an increment of 0.1 ML, where 1 ML corresponds to a thickness of 0.21 nm. Post-annealing of the Er-deposited sample was carried out *in situ* by direct resistance heating. The annealing temperature was monitored by an electric thermocouple.

During the deposition, the (2×1) LEED pattern 'dissolved' gradually into a strong background. Below an Er coverage of 0.4 ML, the (2×1) LEED spots were still bright enough to be identified. At an Er coverage of $\sim$0.6 ML, no LEED spots could be observed at electron energies of less than 100 eV. The fairly quick disappearance of the LEED pattern is indicative of a random uptake of Er atoms on the Si(100) surface at RT.

The Si 2p core level photoemission spectra taken at different Er coverages are shown in figure 1(a). The spectra were taken in the energy distribution curve (EDC) mode with a photon energy of 132.2 eV, which corresponds to a small escape depth of around 0.4 nm for the Si 2p photoelectrons. The high resolution of photoemission enables clear separation of the Si $2p_{3/2}$–$2p_{1/2}$ doublet. For a clean Si (001) surface, the $2p_{3/2}$ component of the doublet is located at a binding energy of 99.22 eV, and a peak at a binding energy of 98.6 eV can be resolved. This peak appears when the LEED pattern shows a (2×1) reconstruction and has been attributed to the Si 2p induced by the surface Si dimers [13]. Its peak intensity decreases with increasing Er coverage, and disappears at a coverage of around 0.6 ML. This
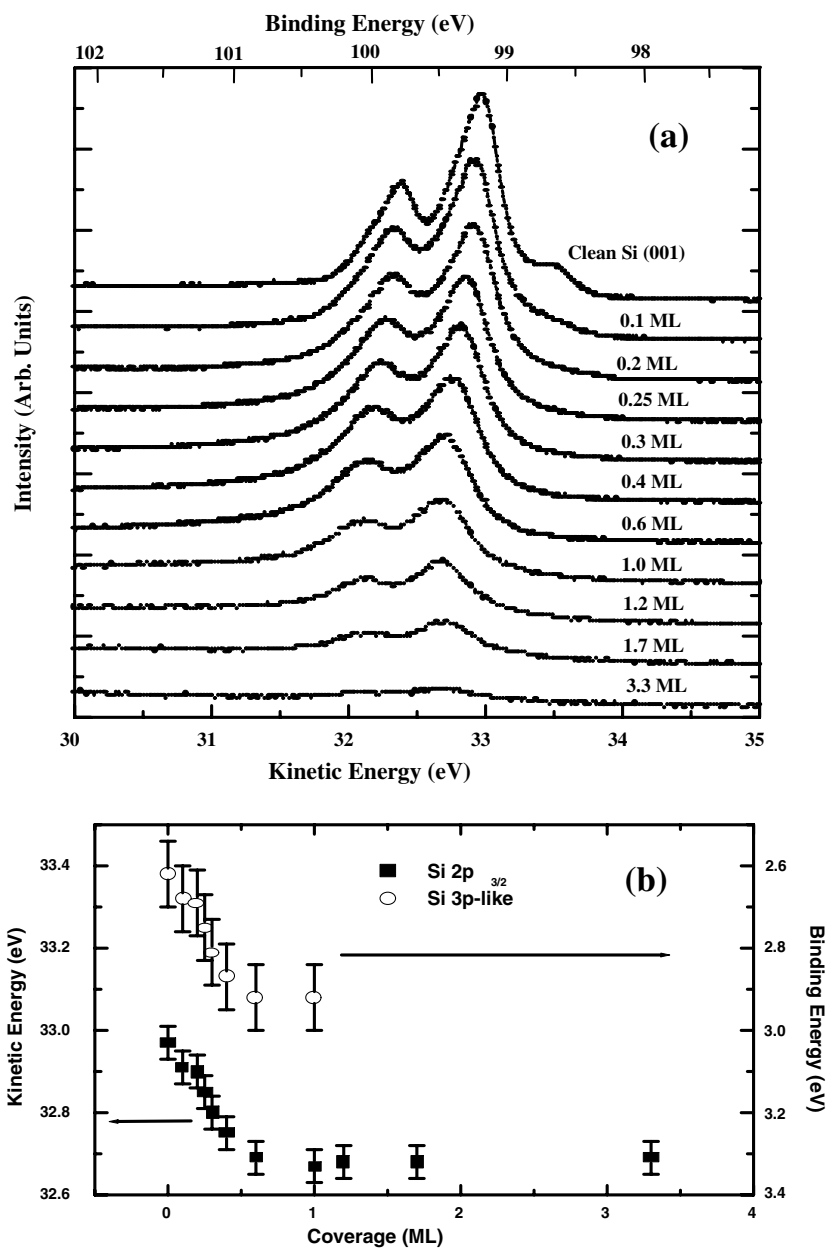
Figure 1. (a) Photoemission spectra of the Si 2p core level for an Er-deposited Si(100) substrate at different Er coverages. The incident photon energy is 132.2 eV. (b) Variation of the Si $2p_{3/2}$ and Si 3p-like peak positions versus Er coverage.

is well consistent with the LEED observation. With increasing Er coverage, no significant change in the Si 2p peak shape could be seen. The curve fitting of the Si 2p peaks based on the convolution of a Gaussian function and a Lorenz function (not shown here) shows that no silicide features could be observed on the higher binding energy side of the main Si 2p peaks. This is consistent with the results of WF measurements by Siokou *et al* [12].

When the Er coverage increases from 0.1 to 0.6 ML, a monotonic shift of Si $2p_{3/2}$ towards higher binding energy is observed. After that, the binding energy of the Si $2p_{3/2}$ signal reaches its maximum at 99.51 eV and keeps rather constant with the continuous increase of the Er coverage to 3.3 ML, as shown in figure 1(b). At this coverage, the Si 2p peaks are almost invisible. The total energy shift for the Si 2p feature with increasing of Er thickness is measured to be 0.29 eV. Meanwhile, the variation of the Si 3p-like valence feature with Er coverage was monitored with the incident photon energy fixed at 26 eV. Almost the same energy shift (about 0.30 eV) of the Si 3p-like feature could be observed as shown in figure 1(b). The same shift for both Si 2p and Si 3p-like features demonstrates that a rigid shift of the core levels exists which may be caused by band bending.

In previous work such a large shift of Si 2p has been observed for the Er/Si(111) interface [5] and many other rare-earth/Si interfaces [14–21]. In the case of rare-earth elements, especially when the coverage is below 0.6 ML, a binding energy shift of about 0.2 eV was observed in almost all of the mentioned papers [15–21], and was generally attributed to a Fermi level shift induced by the rare-earth overlayers, without any obvious chemical reaction to form the silicides. On the other hand, for the Er/Si(111) interface [5], binding energy shifts of 0.5 and 0.7 eV caused by 0.7 and 1 ML of Er overlayers were reported and were attributed to the chemical reaction. With the further deposition of rare-earth element, the silicide-like components appeared and shifted downwards to the lower binding energies. When the coverage reaches around 3–5 ML, the shifts of silicide peaks may saturate at the binding energy of 1.2 eV [17, 18, 20, 21] or 1.3 eV [5, 16, 19] below the bulk Si 2p signal.

Comparing these results with the Si 2p spectra measured at different Er coverages shown in figure 1, one may find that in the ML region the behaviour of Si 2p for the Er/Si(100) interface is similar to that of most rare-earth/Si interfaces except Er/Si(111). For thicker overlayers, however, unlike other rare-earth/Si interfaces, no chemical reaction could be observed for Er/Si(100). Here, we prefer to explain the energy shift in terms of the variation of SBH induced by the shift of the Fermi level [7, 9, 10, 22]. Since no chemical reaction occurs during the deposition, the shift of 0.29 eV of the Si core level to a higher binding energy can be explained by a shift of the Fermi level position within the silicon bandgap and hence by a lowering of the SBH, Φ_{SB}, by an amount $\Delta\Phi_{SB,exp} = 0.29$ eV. On the other hand, the initial value of E_F, which could be regarded as the charge neutrality level (E_{CNL}), is determined to be 0.38 eV by measuring the valence band spectra at 120 eV. Then the final SBH $\Phi_{SB,exp}$ should be equal to the summation of $\Delta\Phi_{SB,exp}$ and E_{CNL}, i.e. 0.67 eV, which is well consistent with the value of 0.68 eV obtained from I/V and photoresponse measurements [23] for the Er/p-Si interface. The difference between the Si 2p peaks for Er/p-Si(100) in this work and that for Er/n-Si(111) in [5] indicates that the charge transfer between Er and Si is more likely to occur at Er/S(111) interfaces than at the Er/Si(100) interface at RT. On the other hand, the shift of SBH induced by the Er overlayer on the n-type Si substrate is rather small (<0.1 eV). This should be also considered in understanding the difference between the Si 2p peaks of Er/n-Si(111) and Er/p-Si(100).

Figure 2 shows the annealing behaviour of the Er/Si sample. Curves (a) and (b) in figure 2 are the Si 2p spectra of the 0.6 ML Er-deposited sample taken before and after 600 °C annealing for 10 min. After annealing, the intensities of the Si 2p doublet increase by about a factor of 2, and their binding energies decrease by about 0.1 eV. In addition, the Si dimer-induced shoulder located at a binding energy of about 0.6 eV below the Si $2p_{3/2}$ peak appears again, which is well consistent with the recovery of the (2×1) LEED pattern. For the 2 ML Er-deposited sample after annealing, except for the dimer-induced shoulder, a weak peak having a binding energy 1.2 eV lower than that of Si $2p_{3/2}$ peak appears, as seen by curve (c) in figure 2. This peak is suggested to be the silicide-induced $2p_{3/2}$ peak, for the following reason: when the
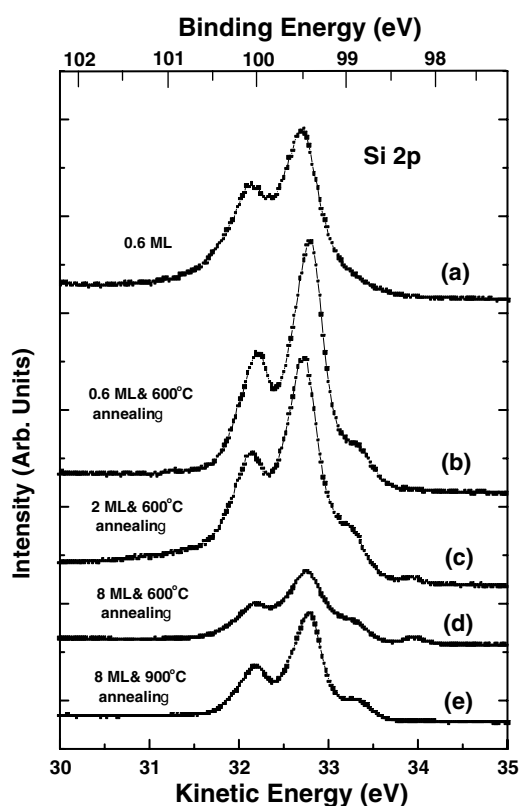
Figure 2. Photoemission spectra of the Si 2p core level for Er-deposited and annealed Si(100) samples at different Er coverages and annealing conditions. The incident photon energy is 132.2 eV.

Er coverage increases to 8 ML, after annealing the intensities of the Si 2p doublet decrease significantly as seen by curve (d), while the dimer shoulder and weak peak still exist. The LEED pattern exhibits a (2×2) structure as shown in figure 3. This pattern has been determined to be a combination of the (2×1) reconstruction from the Si substrate and the $c(2 \times 2)$ reconstruction from the top of the Er silicide islands, based on the results of the LEED and STM observations [24]. The above results demonstrate that the appearance of the weak peak is accompanied with the appearance of a $c(2 \times 2)$ LEED pattern. Thus, it is not unreasonable to attribute the weak peak to the silicide-induced $2p_{3/2}$ peak, while its $2p_{1/2}$ component overlaps the dimer-induced shoulder and is hence not resolved. The coexistence of the dimer and the silicide features indicates that after annealing the sample surface is simultaneously covered by Si dimers and Er silicide. When the original Er coverage is less than 8 ML, the Si dimers may dominate the surface, thus only the (2×1) LEED pattern was observed. When the coverage reaches up to 8 ML, the area occupied by the silicide would be large enough to influence the LEED pattern [24]. By further annealing the sample to 900 °C for 5 min, the silicide peak disappears in curve (e). This implies that full or partial loss of the silicide may occur due to its decomposition at high temperature [11].

The reappearance of the (2×1) pattern is evidence that after annealing the Er diffuses into the Si substrate and reacts with the outermost few layers of Si atoms to form the silicide [5]. The experiments show that relatively large surface areas of the sample are exposed to the Si
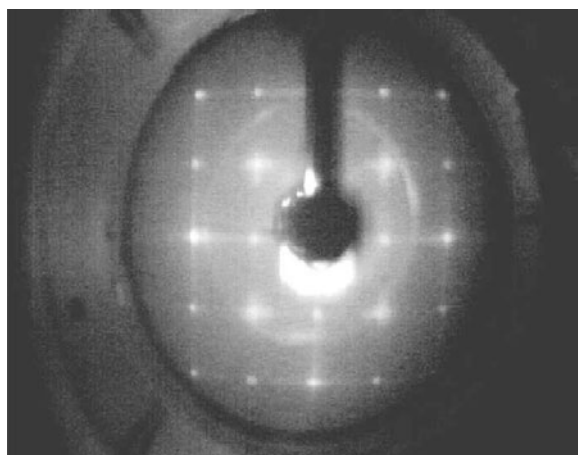
Figure 3. LEED pattern of a '(2 × 2)' surface. The fractional order spots (±1/2, ±1/2) show
different focusing with other spots, indicating that they are from a c(2 × 2) surface. The other spots
can be made into a (2 × 1) + (1 × 2) reconstruction.

dimers after annealing. In curves (c) and (d) of figure 3, the ratios of the intensities of the
dimer-related peak to the bulk peak are estimated to be 0.33 and 0.40 respectively. They are
rather close to each other, indicating that the area occupied by the dimers does not change very
much with the variation of Er coverage.

As for the silicide-induced peak, its energy position keeps quite stable for different Er
coverages. In previous studies on many other rare-earth/Si interfaces, the downward peak
shift with respect to the bulk Si 2p doublets for the binding energy of 1.2 or 1.3 eV has been
observed and determined to be induced by the silicide [5, 16–21]. This comparison may provide
a further reason for us to assign the 1.2 eV-shifted peak to a silicide-induced peak. The peak
shift shown here is different from that observed for the Er/Si(111) interface, in which the peak
shifts caused by silicides have been reported to be 0.54 eV for $ErSi_2$ and 0.36 and 0.65 eV for
Er_3Si_5 [7, 9, 10]. There is no definite evidence that these three components could be resolved
from our Si 2p spectra by deconvolution, since our SRPES spectra possess a relatively high
resolution. We suppose that the difference might come from the different crystalline structures
of silicides. $ErSi_2$ and Er_3Si_5 phases are all of the AlB_2 type hexagonal structure, while in
our case the crystalline structure of silicide on Si(100) was found to be the tetragonal $ThSi_2$
type [25]. The different chemical environments of Si in the different silicides might lead to
the difference in the core level shifts between Er/Si(111) and Er/Si(100) interfaces. Of course
further evidence is needed to confirm or deny this postulation.

Figure 4 shows the Er 4f core level and Si valence band spectra taken at an incident photon
energy of 175 eV, at which the Fano resonances between 4f → continuum and 4d → 4f occur,
so that the intensity of Er 4f reaches its maximum. For a clean Si(100) surface without Er
deposition, the typical Si 3s–3p hybridized and 3p-like features are shown in curve (a). The
latter is located in the energy range of −5 eV to the Fermi level with a prominent peak at
−2.9 eV. Curves (b)–(d) correspond to the 0.6, 2 and 8 ML Er-deposited samples followed
by 600 °C annealing respectively. Curve (e) is the spectrum of a 30 ML Er-deposited sample,
which could be viewed as the spectrum of bulk Er. As the thickness of deposited Er increases,
the intensity of the Si valence spectrum decreases gradually and the Er 4f feature dominates
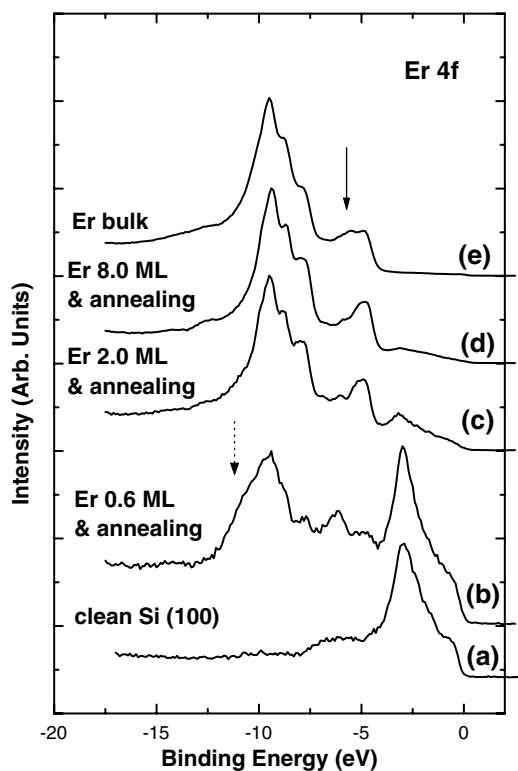the spectrum. In curve (b), the dotted arrow points to a shoulder located at the binding energy

Figure 4. Photoemission spectra of Er 4f core level and Si valence band structures for a clean Si(100) substrate and Er-deposited samples with different Er coverages and annealing conditions. The incident photon energy is 175 eV.

of 1.2 eV below the main Er 4f features in the binding energy range of 12–6 eV. This origin of this shoulder has not yet been confirmed.

The main Er 4f features in curves (c) and (d) are quite similar to those in curve (e), while small differences in the Er $^5I_8$ feature can be noted. Such a difference between the bulk Er and the Er silicide has also been observed on the Si(111) surface, as reported by Wetzel *et al* [5], and has also been explained by the coexistence of surface and bulk features in the 4f spectrum of a thick Er sample, while the surface feature would not appear in the case of the silicide. On the other hand, the sharpening of the $^5I_8$ after annealing also provides evidence that a monospecies of Er silicide may exist on the surface.

In summary, the information extracted from Si and Er core level and Si valence band photoemission spectra has permitted a rather detailed description of Er/Si(100) interface formation. The results can be summarized as follows. The pinning of the surface Fermi level at 0.29 eV above its initial value, equivalent to an SBH of 0.67 eV, is observed upon deposition of ∼0.6 ML Er onto a clean p-type Si(100) (2 × 1) surface at RT: no evidence is found for the formation of Er silicides at the as-deposited surfaces. Annealing of the Er-covered Si(100) surfaces at 600 °C results in the appearance of a new component with a 1.2 eV energy shift towards lower binding energy in the Si 2p core level spectrum, which is indicative of the presence of some sort of Er silicide. Meanwhile, the Er 4f spectrum measured upon annealing exhibits a well-resolved fine structure, which implies that only monospecies of Er silicide may exist on the surface.

Acknowledgments

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