Domain wall structures in an ordered Si/Fe(110) surface alloy
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Abstract
During the annealing process of an Fe_{96.5}Si_{3.5}(100)/(110) bicrystal, silicon and impurity carbon segregate to the surface. The structures formed by the segregands on the (110) surface have been studied by STM (geometry) and AES (chemical information). Silicon substitutes iron surface atoms and forms a two-dimensional alloy, whereas carbon occupies hollow sites in the first monolayer, leading to a distortion of the substrate lattice. The structures are based on a c(1 × 3)Si 0 = 1/3 ordered surface alloy. Additional silicon as well as the co-segregating impurity carbon are inserted into this structure by formation of domain walls. If the density of these nearly straight and parallel domain walls becomes high enough, commensurate domain wall structures with c(1 × n) supercells can be observed.

Keywords: Iron; Low index single crystal surfaces; Scanning tunneling microscopy; Silicon; Surface segregation; Surface structure

1. Introduction
Segregation of silicon and impurities on iron silicon alloy surfaces and grain boundaries has been studied intensively because of its essential impact on technologically important phenomena like temper embrittlement and corrosion of steel. Single crystal surfaces provide a simple model system to study surface segregation [1,2].

The segregation of carbon and silicon exhibits a strongly temperature dependent competition for surface sites. At high temperatures silicon is the dominant segregand, due to its high bulk concentration. Below a certain temperature, depending on the bulk concentrations, silicon is displaced more and more by carbon, whose segregation enthalpy is significantly larger than that of silicon [3–5].

Combined LEED (low energy electron diffraction) and AES studies of the (100) surface report a c(2 × 2) ϑ = 1/2 saturation superstructure for most impurity segregands and silicon [3,4] as well. Concerning the nearly closed packed (110) surface only few structural data are available. A c(1 × 7)Si superstructure was found by means of LEED on Fe_{x}Si_{1−x}(110) x = 1–10 at% samples [3,6–8] at silicon surface concentrations ranging from 6.5 to 33% [6–8] and 35% [3], respectively, determined by AES.

2. Experimental
The measurements were carried out in UHV at a pressure typically below 5 × 10^{-11} mbar with a
Fig. 1. (a) 10 × 10 nm STM topograph of the (110) c(1 × 3)Si,C \( \theta_{Si} = 31\% \quad \theta_{C} = 6\% \) surface. Only the iron atoms are visible. The nearly vertical domain boundaries (white line) are caused by co-segregated carbon atoms, which are assumed to occupy interstitial sites. The four short white lines indicate the displacement of the iron atoms neighbouring the boundary. They would be equidistant in the undistorted lattice. (b) Schematic model of the detail marked in the STM image.
commercial STM (Omikron μ-STM) at room temperature. The tip was electrochemically etched from tungsten wire and cleaned in UHV by sputtering with 1 keV Ar\(^+\) ions.

The sample, an Fe 3.5 at% Si bicrystal, allows the investigation of a (100) and a (110) surface, which are separated by a single grain boundary. The surface was cleaned by sputtering with 1 keV Ar\(^+\) ions. Upon annealing mainly silicon and impurity carbon diffuse to and segregate on the surface. This process is interrupted after some minutes by cooling down to room temperature to allow the STM study of the frozen surface structure. Annealing below 750 K yields carbon surface concentrations up to 20%. Using higher annealing temperatures (750 to 1000 K) after carbon depletion of the surface layer by sputtering at cyclically varied temperatures (450–700 K) for several hours, a carbon free and silicon saturated surface could be prepared.

The surface composition was routinely controlled by AES measurements. The Si Auger-sensitivities were gauged using the known 50% equilibrium concentration of the (100) c(2 × 2) silicon saturated surface [3]. Carbon impurities on the surface were quantified by multiplying the C(273 eV)/Fe(703 eV) APPH ratio (Auger peak-to-peak height) by a factor of three. This factor was calculated using an Auger quantification procedure [9] based on the work of Shimizu [10] and du Plessis [11] with Auger sensitivities and electron inelastic mean free paths given in Refs. [12,13].

### 3. Results and discussion

Annealing the sputtered sample for two minutes at 750 K shows the segregation process on the (110) surface in an early stage with about 15 at% silicon surface concentration. The silicon atoms appear as 10–20 pm deep disordered depressions in the iron substrate [14]. Longer annealing (10 min at 750 K) leads to a virtual saturation of the silicon surface concentration at 36 at% determined by AES in accordance with a similar result of 35 at% in Ref. [3]. The atomically resolved STM image (Fig. 1) shows a c(1 × 3) superstructure apparently formed by nearly hexagonal rings of atoms. These structures are separated into domains by boundaries crossing the image from top to bottom. These boundaries have been found to depend on the concentration of co-segregated carbon and are discussed below.

The first question arising concerns the structure and site of the segregated silicon atoms. The hexagonal ring pattern can be obtained if 33% of the surface iron atoms of the perfect surface lattice are invisible (the holes in the hexagonal rings). Since the amount of these invisible atoms matches the surface concentrations of silicon derived by AES quite well, it is evident that the missing iron atoms are hidden or displaced by silicon atoms, in accordance with their appearance as depressions in the images at low coverages.

Although the symmetry of the STM image would allow both substitutional or on-top sites for Si, the latter possibility can be ruled out for the following reasons: (a) It generally is not plausible that a chemisorbed adsorbate occupies on top sites, if there is enough space for an arrangement using exclusively hollow sites. The surface Si–Si distance in the c(1 × 3) structure (0.48 nm) is twice as large as typical bulk Fe\(_x\)Si\(_{1-x}\) interatomic Fe–Si distances (0.24 nm). (b) Adsorbed atoms, except some electronegative and rare gas adsorbates, should appear as protrusions rather than depressions in on top positions on jellium-like surfaces (closed packed metal surfaces), regardless the underestimation of the real atomic size by the STM [15]. (c) Si occupies substitutional sites both in the bulk and on the Fe(100) surface [16].

The c(1 × 3) structure is different from all {110} planes of the known Fe\(_x\)Si\(_{1-x}\) ordered bulk structures. So it cannot be understood as a surface induced bulk-like ordering of the topmost monolayers. Consequently the structure may be called a two-dimensional alloy comparable to surface alloys formed in typical metal on metal systems with miscible components like Cu(100) c(2 × 2)Au [17]. This is supported by our AES measurements using the 1620 eV KLL peak of silicon, which has a probing depth of several monolayers. The resulting concentration in the first monolayer, assuming 3.5 at% Si bulk concentration already in the second monolayer, is compatible with the discussed structure.

The STM images of the extensively prepared carbon free Si/Fe surface were expected to exhibit a perfect c(1 × 3) superstructure (Fig. 4b) without car-
bon induced boundaries. Nevertheless, apart from the c(1 × 3)Si structure, again domain boundaries can be seen (Fig. 2a). Bearing in mind that the dark spots represent the Si atoms, it is obvious that the Si–Si distance in the boundaries is lower than in the c(1 × 3) supercell, resulting in an increase of the surface concentration above 33.3% of the perfect c(1 × 3) structure (Fig. 4b). The density of these ⟨110⟩ directed boundaries increases by annealing at higher temperatures. Thus they are not imperfections due to kinetic limitations of the segregated Si atoms, but necessary to incorporate additional segregated silicon atoms into the surface. Hence the Fe(110) c(1 × 3)Si surface does not represent a saturation superstructure like, e.g., the silicon saturated Fe(100) c(2 × 2)Si structure [3].

These boundaries constitute an equivalent to the domain wall structures well known from several (non substitutional) chemi- and physisorption systems like H/Fe(110) [18,19] or Xe/Pt(111) [20]. Domain wall structures are a typical reaction of an ordered adsorbate structure to increasing coverages in the case of repulsive nearest neighbour interactions of the adsorbed atoms. The individual domain
walls themselves repel each other due to elastic and dipole interactions [21]. Domain walls behave similar to monatomic steps. They also form kinks and show a roughening transition, i.e., at sufficiently low temperatures domain walls become straight, whereas they are rough (meandered, kinked) above a critical temperature [21]. If the average distance of the straight walls coincides with the substrate lattice, commensurate domain wall structures with a well-defined superstructure unit cell may occur. The structure with meandered walls is called incommensurable since the walls are continuously moveable (by kinks moving along the wall) which destroys any long-range order [21].

The walls in the STM image (Fig. 2a) appear indeed meandered, characteristic of a wall structure above its roughening transition, which has been frozen in during the cooling process (STM at room temperature). At silicon coverages around 38% small domains of a c(1 x 5)Si \( \theta = 40\% \) commensurate structure have been observed, where several walls touch each other (Figs. 2b and 4a). A correlation analysis of the domain wall structure (Fig. 2a) yields a significant repulsion among the walls [14]. Consequently the formation of the commensurate superstructures does not represent the condensation and growth of a new phase. On the contrary it is rather of a continuous nature, caused by the increasing density of the homogeneously distributed domain walls.

The density of the second type of domain boundaries, which are visible in Fig. 1 scales with the carbon surface concentration obtained by AES. Two details concerning these boundaries are remarkable: (a) A complete \( \langle 110 \rangle \) row of Fe atoms (type B in Fig. 1b) in the centre of the boundary is nearly invisible. (b) The iron atoms (type A) in the two neighbouring \( \langle 110 \rangle \) rows are significantly displaced, either apparently by the influence of the carbon atoms on the electronic structure, or more likely by real topological distortions.

Both effects qualitatively occur also on the C/Ni(100) surface and can be explained by carbon atoms in surface interstitial positions. On fcc Ni(100), carbon occupies four-fold hollow sites nearly in-plane with the surface. To enlarge the available space an in-plane rotation of the Ni atoms around the penetrating carbon atom is induced [22]. On Fe(110) the carbon atoms seem to displace their iron neighbours in \( \langle 100 \rangle \) direction (type A) in order to transform the originally two-fold hollow site into one with nearly four-fold symmetry (Fig. 1b). On Ni(100), besides the topological distortion, carbon locally reduces the density of states of its very Ni neighbours significantly, leading to a reduction of the apparent height up to 70 pm for a Ni atom with 2 carbon neighbours [23]. Assuming chains of interstitial carbon atoms in the centre of the boundaries, where each iron atom is neighboured by two carbon atoms, the disappearance

Fig. 3. 10 x 5 nm STM topograph showing the carbon-induced commensurate c(1 x 5) \( \theta_{Si} = 30\% \) \( \theta_{C} = 10\% \) domain wall structure. The white lines mark the centres of the domain walls (carbon chains).
visible iron atoms dissolve to the ring and ladder structures visible in the image in Fig. 3.

To conclude, segregated silicon has been found to occupy substitutional sites in contrast to the adatom adsorption sites of typical non-metal segregands or adsorbates. The arrangement of segregated carbon and silicon on the Fe(110) surface is characterized by domain wall structures based on a c(1 × 3)Si surface alloy. They allow a continuous variation of the surface composition without appearance of coexisting phases (e.g., a pure carbon phase coexisting with a pure silicon phase). Depending on the preparation conditions a great variety of c(1 × n) commensurate domain wall structures can be observed, especially with c(1 × 5)Si and c(1 × 5)Si,C and c(1 × 7)Si,C supercells.

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References