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Chemical identification of atoms at multicomponent surfaces on an atomic scale: $CoSi_2(100)$

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We found a $(\sqrt{2}\times\sqrt{2})R45°$ surface reconstruction on the plateau of three-dimensional cobalt silicide islands epitaxially grown on Si(100), which has an inhomogeneous occupation of the lattice sites. We combined voltage dependent scanning tunneling microscopy with *ab initio* electronic structure calculations and resolve the chemical identity of the surface atoms. We found that Co atoms are imaged for bias voltages probing the unoccupied states above +0.5 eV and vice versa, Si atoms are imaged below +0.5 eV, counterintuitive to the simple interpretation based on the electronic structure of bulk Co and Si. [S0163-1829(97)51420-2]

The scanning tunneling microscope (STM) is now used routinely to image, for instance, semiconductor surfaces down to the atomic resolution. In one-component systems, the STM has given valuable information on the atomic structure of semiconductor surfaces.[1] In multicomponent systems, where two or more different chemical species are expected at the surface, the chemical identification on the atomic scale turned out to be more difficult. For some binary systems like GaAs (Ref. 2) or Al on Si(111) (Ref. 3), STM measurements at different bias voltages or spectroscopic measurements proved to be successful. However, for other systems like Ge/Si, the silicides or the perovskites, the chemical identification atom by atom is an open problem.

The surface of $CoSi_2$ presents a case study for this type of problem. Due to the specific requirements of growing flat silicide layers[4–6] or growing silicide islands[7] on Si(100), for applications of silicides in microelectronic devices, a detailed knowledge of growth and structure is desirable. $CoSi_2$ is the best investigated silicide surface at all, but no clear conclusion on the chemical nature of the surface structure exists.

$CoSi_2$ crystallizes in the CaF_2 lattice structure, characterized by adjacent (100) lattice planes stacked along the [001] direction alternately occupied with eight Si or four Co atoms. Correspondingly, two different bulk terminated surface structures exist: a Si and a Co terminated one. Experimentally it was found that both surfaces reconstruct. The Co-rich surface (C surface) was found to be $(\sqrt{2}\times\sqrt{2})R45°$ reconstructed. In models reported for this C surface, one monolayer (ML) of Si resides on top of the Co layer.[6,8–10] A structural model of the C surface is shown in the top right part of Fig. 1.[11] The Si-rich surface (S surface[12]) shows also a $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction with 1.5 ML Si on top of the upper Co layer illustrated in the top left part of Fig. 1.[6,9] A recent STM study shows that the C surface has a complete occupation of the lattice sites and only the S surface has an incomplete one.[6]

In this paper, we compare atomically resolved STM images of $CoSi_2$ islands, taken at different tunneling voltages, to the lateral distribution of the energy integrated local density of states, obtained from self-consistent *ab initio* calculations. We find that this comparison resolves the chemical nature of the protrusions observed in the STM images. When we image the surface applying a sample bias voltage U_B larger than $\sim +0.5$ V above the Fermi energy (E_F), the observed protrusions can be assigned to Co atoms. On the other hand, when we image with bias voltages lower than $\sim +0.5$ V, the observed protrusions can be assigned to Si atoms. This is exactly opposite to simple arguments based on

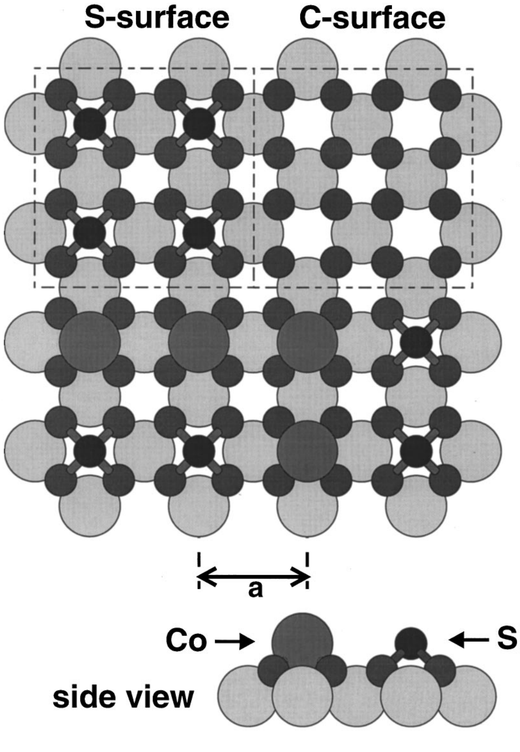

FIG. 1. Structural models of different terminations of $CoSi_2(100)$. Models for the S-terminated and C-terminated surfaces are shown in the left and right dashed squares in the top, respectively. In the lower part of the top view a model of a mixed surface termination is shown. Part of the surface is S terminated in the other part of the surface the top Si atom is replaced by a Co atom (cf., side view).

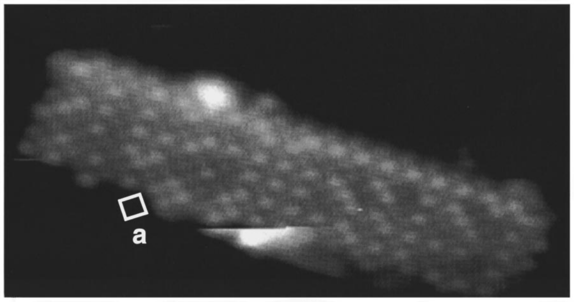

FIG. 2. Atomically resolved image of the top facet of a silicide island. (1.5 ML Co deposited, $T_{Si}=500\,°C$, $U_B=+1.2$ V, $I=200$ pA.) The surface unit cell is indicated corresponding to a $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction. Only 50% of the lattice sites are occupied by atomic protrusions shown as bright dots.

the bulk density of states of Co and Si. These results show, (i) that the combination of voltage dependent STM measurements and *ab initio* electronic structure calculations open the possibility to identify the chemical nature of the atoms observed in STM images, and (ii) we propose a model with an inhomogeneous occupation of the surface lattice sites by Co or Si atoms.

The STM experiments were performed at room temperature in the constant current mode with a tunneling current of several 100 pA and typical bias voltages between −2 V and +2 V were applied to the sample. To study the bias voltage dependence of the STM images, we use the following procedure: Each scan line is recorded up to six times with up to six different sample bias voltages. This way, we scan six images simultaneously with six different bias voltages. Here we used 0.3 V, 0.6 V, 0.9 V, 1.2 V, 1.5 V, and 1.8 V. For the negative polarities we took another six images.

The silicide films were prepared by reactive deposition epitaxy, i.e., depositing 1.5 ML of Co with the Si(100) sample held at a temperature of 500 °C. It was shown earlier, that under such conditions, formation of $CoSi_2$ occurs.[10] We observe formation of three-dimensional (3D) islands with aspect ratios (length /with) of 3 . . . 5 and heights of ~15 Å.[13] The morphology of these 3D islands is described in detail in Ref. 13. Some of these silicide islands have flat tops. In the following, we will concentrate on the structure of the top facets of these islands.

Figure 2 shows an atomically resolved STM image of the plateau of a 3D island ($U_B=+1.2$ V). The atomic protrusions, shown as bright spots, are located on a square lattice with a periodicity of 5.5 Å along the ⟨110⟩ directions of the substrate. The unit cell of this reconstructed surface is $\sqrt{2}$ times longer in linear dimension and rotated by 45° relative to the underlying Si substrate. This shows that, experimentally, a $(\sqrt{2}\times\sqrt{2})R45°$ reconstructed lattice is observed by STM. However, this reconstruction lattice seems not to be occupied completely. For about 50% of the lattice positions in Fig. 2, no atomic protrusions are observed. Stalder *et al.*[6] observed a similar behavior. They interpreted the incomplete occupation of the lattice sites as vacancy defects.

To analyze the reason for this incomplete occupation of the lattice sites in detail, we performed voltage dependent STM measurements. In Fig. 3(a) we show another atomically resolved STM image of the top plateau of a silicide island ($U_B=+1.2$ V). Also on this island a $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction lattice is present. In Fig. 3(a) 25% of the lattice positions are occupied by bright protrusions. When we change the sample bias voltage from +1.2 V in Fig. 3(a) to +0.3 V in Fig. 3(b), we observe that different lattice sites are displayed as bright protrusions. A detailed comparison of the images shown in Figs. 3(a) and 3(b) shows that both images are complementary in the sense that the lattice sites, on which bright protrusions are present at a $U_B=+1.2$ V, have no protrusions at $U_B=+0.3$ V and *vice versa*. This complementary behavior with respect to the occupation of the lattice sites is also illustrated in Fig. 3(c), which displays the sum of the images in Figs. 3(a) and 3(b), for which an atomic protrusion is present at every lattice site.

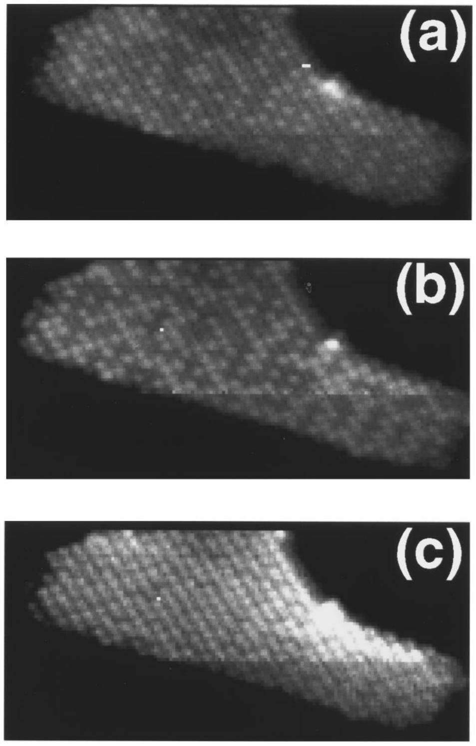

FIG. 3. The top facet of a silicide island is shown in (a) and (b) imaged at +1.2 V and +0.3 V sample bias voltage, respectively ($I=150$ pA). Complementary sets of lattice positions are imaged as bright protrusions at the different bias voltages. The sum of (a) and (b) is shown in (c). Now all lattice positions are imaged as bright protrusions.

The general trend with respect to the voltage dependence of the images is as follows: At bias voltages of +0.6 V and higher, the same lattice sites always show bright protrusions, and for bias voltages of +0.3 V and lower (and for negative bias voltages), the complementary set of lattice positions is imaged as bright protrusions. This voltage dependence of the observed corrugation at different lattice sites precludes a purely morphologic nature of the observed image contrast. Therefore, vacancy defects are excluded as a reason for the observed incomplete occupation of the lattice sites and we propose a model with an inhomogeneous occupation of the surface lattice sites by Co and Si atoms. The model is based on the S surface, which has a 1.5 ML Si on top. In our model a certain amount of the top Si atoms are replaced by top Co atoms (cf., bottom of Fig. 1).

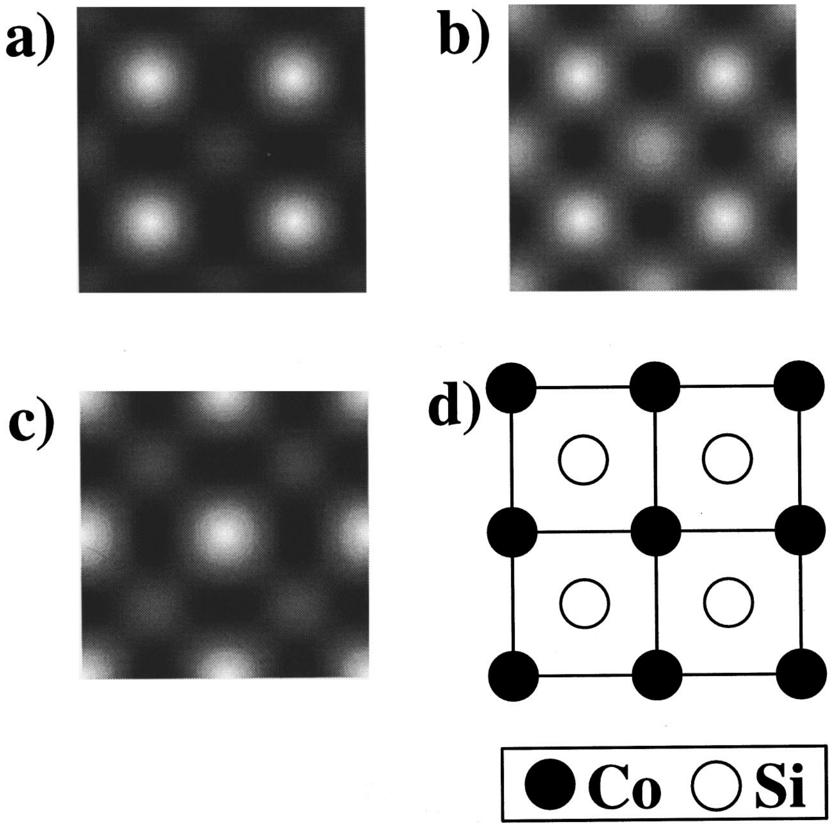

FIG. 4. Calculated lateral distribution $\mathbf{r}_\parallel$ of the ILDOS $\int n(\mathbf{r}_\parallel, z_0|E)dE$ at a distance of $z_0 = 7$ Å from the center of the surface atoms. The panels show integrals over different energy ranges: (a): -0.1 to 0 eV, (b): 0 to $+0.5$ eV, (c): 0 to 1.0 eV, (d) shows the surface unit cell with Co shown as solid circles and Si as open circles.

In order to prove our model, we aim to relate the voltage dependent behavior of the STM images to the chemical identity at the $\mathrm{CoSi_2}(100)$ surface by performing electronic structure calculations based on the density-functional theory in the local-density approximation.[14] The results are obtained with the full-potential linearized augmented plane-wave method[15] for film geometry. *Ab initio* calculations for an inhomogeneous distribution of Co and Si surface atoms, as proposed in our model, are at present unattainable. To simulate a mixed termination, with Co and Si atoms randomly distributed at the lattice positions of the $(\sqrt{2} \times \sqrt{2})R45°$ reconstructed surface, we use a $c(2 \times 2)$ unit cell with an equal amount of Si and Co at the surface. We think that this is a good structural model, since the STM images show little difference in the brightness when nearest-neighbor atoms are of the same kind. We have chosen a nine layer film consisting of seven layers bulk $\mathrm{CoSi_2}$ made up of an alternating sequence of four Co or eight Si atoms per layer. We have chosen the experimental lattice constant of 5.356 Å. Structural relaxation are not taken into account.

We calculated the lateral variation $\mathbf{r}_\parallel$ of the local density of states (LDOS) $n(\mathbf{r}_\parallel, z|E)$ at several distances z (3–11 Å) from the surface. According to the approximation by Tersoff and Hamann,[16] the variation of the tunneling current with bias voltage U_B is proportional to the LDOS of the sample at the tip position $\mathbf{r}_0$, $dI/dU_B \propto n(\mathbf{r}_0|E_F + eU_B)$. Thus the energy integrated LDOS (ILDOS) of occupied $(U_B < 0)$ or unoccupied $(U_B > 0)$ states in the energy range $(E_F, E_F + eU_B)$ contribute to the tunneling current, $I(\mathbf{r}_0) \propto \int_{E_F}^{E_F+eU_B} n(\mathbf{r}_0|E)dE$, and can be directly compared with the gray scale plots of constant current STM images.

Figure 4 shows gray scale plots of the LDOS integrated over energy intervals characteristic for different STM images

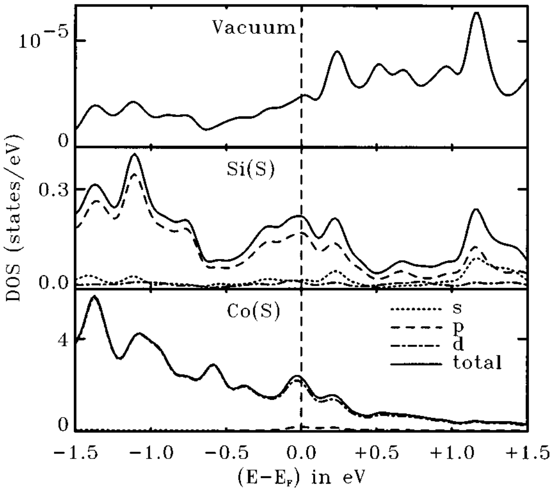

FIG. 5. Top panel shows the vacuum DOS $n(E)$, integrated over $\mathbf{r}_\parallel$ of the surface unit cell and integrated over a slice 5.7 Å $< z <$ 6.8 Å measured from the center of the surface atoms. The origin of the energy scale is positioned at E_F. Middle and bottom panel show the LDOS of Si and Co, respectively, within the surface muffin-tin sphere.

observed. For energies corresponding to tunneling voltages probing the occupied states, the image is dominated by large ILDOS located at the position of the Si atoms. The ILDOS does not change much for bias voltages in the range between -1.5 eV and E_F, and Fig. 4(a) provides a typical example at $U_B = -1.0$ eV. Even for tunneling voltages probing the unoccupied states up to close to $+0.5$ eV, the ILDOS remains nearly unchanged. At about $+0.5$ eV above the Fermi level, an approximately equal amplitude of the ILDOS is calculated at the positions of the Co and the Si atoms [Fig. 4(b)]. For higher energies, $E > +0.75$ eV, a contrast reversal is observed and the largest ILDOS is observed at the positions of the Co atoms [Fig. 4(c)]. This type of image remains nearly unchanged up to an energy of about $+1.2$ eV, then the ILDOS located at the Si site recovers partly. This leads to a smaller corrugation between Si and Co atoms.

Comparing these results with the STM images, we find that the theoretically predicted and experimentally observed contrast reversal at a tunneling voltage of about $+0.5$ V agree very well. Combining the STM results with the *ab initio* calculations, we assign the protrusions observed for tunneling voltages below $\sim +0.5$ V to Si atoms and the ones observed above $\sim +0.5$ V to Co atoms.

This assignment is opposite to the intuition based on the simple arguments derived from the LDOS of bulk Co and Si.[14] For Co we find a large LDOS within ± 0.5 eV, i.e., within the vicinity of E_F, while Si shows a band gap in this region. Therefore, it is expected that mainly Co states contribute to STM images at energies below $+0.5$ eV, and the observed STM image is thought of probing the Co states rather than the Si ones. An understanding of the STM images on the basis of the electronic structure is provided by the LDOS shown in Fig. 5. Although for $E < E_F$ the DOS is clearly dominated by Co, the vacuum LDOS integrated over a range of 5.7 Å$<\Delta z<$6.8 Å follows the Si LDOS. This is due to the orbital character for the different atoms. For an energy interval between about -1 eV and E_F, the Si states are of p_z character and extent further into the vacuum than the Co d_{zx} and d_{zy} states. For positive energies we find a peak at about 0.2 eV in the vacuum, Si and Co LDOS, which is due to p_z and $d_{zx,y}$ states localized at the Si and Co surface atoms, respectively, leading to the same ILDOS as for the occupied states. For energies between 0.4 eV and 1.0 eV the LDOS of Si is very small, but the vacuum LDOS shows several bumps. These are due to Co states and the states between 0.5 eV and 0.75 eV are responsible for the contrast reversal. The energy integrated (0.5 eV$<E<$0.75 eV) LDOS $n(r)$ shows that these states are of d_z^2 character and dominate the STM image. At 1.2 eV we find a peak in the vacuum LDOS that is basically of Si-sp character reducing the corrugation in the STM image at larger bias voltages.

Summarizing, we used voltage dependent scanning tunneling microscopy to study the plateaus of 3D cobalt silicide islands epitaxially grown on Si(100). We found a $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction, which has an inhomogeneous occupation of lattice sites. Voltage dependent measurements show, that the occupation of the lattice sites is complementary for different tunneling voltages. A contrast reversal was found at about 0.5 V. *Ab initio* calculations reproduce the voltage dependence of the STM image including the contrast reversal at 0.5 eV and provide the chemical resolution of the STM image. We think that voltage dependent STM combined with *ab initio* calculations provide a powerful strategy to identify different chemical species at the surface of multicomponent systems on an atomic scale.

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[11] The model of the C surface shown in Fig. 3 is (1×1) terminated. For the sake of simplicity the relaxations towards the $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction are not shown, cf., Ref. 12.

[12] We would like to point out that although the terminology ''C and the S surface'' is widely used and we refer to this terminology in this paper, it is misleading, because both, the C and the S surface are known to be Si terminated, the C surface with 1 ML Si and the S surface with 1.5 ML Si.

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