

Ring Clusters in Transition-Metal–Silicon Surface Structures

P. A. Bennett

Physics Department, Arizona State University, Tempe, Arizona 85287

M. Copel, D. Cahill,^(a) J. Falta, and R. M. Tromp

IBM Research Division, T. J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 21 November 1991; revised manuscript received 19 May 1992)

We have determined the atomic structure of the Si(111)-($\sqrt{7}\times\sqrt{7}$)Co surface using scanning tunneling microscopy and ion scattering. The unit cell contains one surface substitutional cobalt atom centered under a 6 silicon adatom cluster. High-temperature annealing produces a low density lattice gas of these ringlike clusters, giving rise to an “impurity stabilized 1×1 ” structure. They occur for several other transition metals, suggesting a stable, universal, silicide related structure.

PACS numbers: 68.35.Bs, 61.16.Di

The atomic geometry of transition-metal- (TM-) silicon structures at surfaces and interfaces is an issue of both practical and fundamental interest. On the practical side, TM silicides offer high-temperature materials for silicon metallization as well as rectifying junctions with a variety of Schottky barrier heights [1,2]. On the fundamental side, TM silicides offer single-crystal epitaxial overlayers, from which the ideal properties of metal-silicon interfaces can be probed [3]. The presence of unfilled *d*-electron shells in these materials presents a particular theoretical challenge [4–6].

Several superlattice reconstructions have been observed in TM-Si(111) systems [7–9], yet the atomic structure of none of these is known. Most TMs display strongly exothermic reactions with silicon, forming a variety of silicides with a propensity for epitaxy [10]. These observations suggest that TM-silicon surface reconstructions may involve radical rearrangements of atoms, as opposed to simple decoration of the substrate.

In this work, we have determined the atomic geometry of the Si(111)-($\sqrt{7}\times\sqrt{7}$)Co and “(cobalt) impurity stabilized 1×1 ” structures using the complementary strengths of scanning tunneling microscopy (STM) and medium energy ion scattering (MEIS). The structure involves substitutional metal atoms and clusters of silicon adatoms in bridge-bonded sites, with a low overall density of dangling bonds. The same structure occurs for several different TMs. As such, it provides fundamental insight into TM-silicon bonding in an environment of reduced coordination.

The Si(111)-($\sqrt{7}\times\sqrt{7}$)Co surface was prepared by depositing ~ 0.1 ML Co (1 ML = 7.83×10^{14} atoms/cm²) onto a clean Si(111)-(7×7) surface and annealing to 670°C. This produces a ($\sqrt{7}\times\sqrt{7}$)R19.1° structure (referred to below as $\sqrt{7}$) coexisting with patches of the clean (7×7) surface [11]. The low-energy electron diffraction (LEED) pattern shows broad $\sqrt{7}$ spots, corresponding to small ordered domains (~ 50 Å), in agreement with the STM images. In Fig. 1(a) we show an empty states STM image of the $\sqrt{7}$ surface. The surface unit cell is outlined, and contains one trigonal structure

with maxima directed along the $\langle 110 \rangle$ azimuths. In the matching unit cell of the filled states image [Fig. 1(b)], a single maximum is observed, centered between the lobes of the empty states. The $\sqrt{7}$ unit cell can occur with two distinguishable orientations, rotated 19.1° relative to the substrate. Whereas each unit cell displays three distinct maxima at positive bias in the interior of a $\sqrt{7}$ domain, this threefold symmetry is less pronounced at domain boundaries and edges. Isolated unit cell clusters have a ringlike appearance, similar to a tiny, well-formed bagel.

Figure 1(c) shows an empty states image obtained on a $\sqrt{7}$ sample subjected to annealing at 1250°C. The LEED pattern from this structure is (1×1), corresponding to the so-called “impurity stabilized 1×1 ” surface

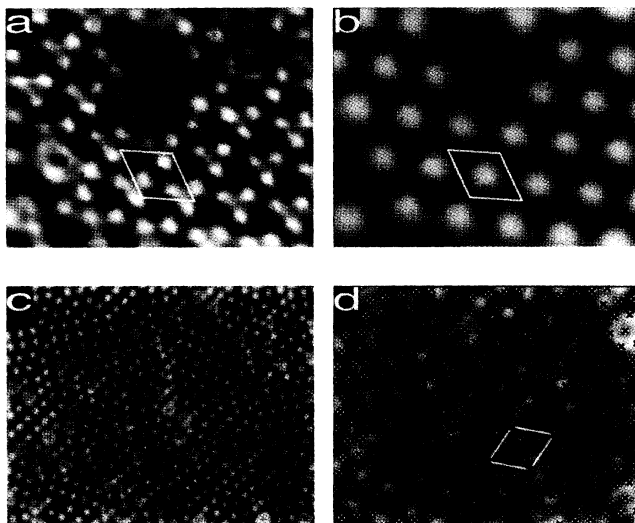


FIG. 1. STM images of Co adsorbed on Si(111). (a) Empty states image (+2.0 V) of the $\sqrt{7}$ surface with a single unit cell outlined. Trimer lobes point in $\langle 110 \rangle$ azimuths. (b) Matching filled states image (−1.8 V). (c) Empty states image (+2.2 V) of the (cobalt) “impurity stabilized 1×1 ” surface. It is a lattice gas of the clusters coexisting with silicon adatoms. (d) Like (c), at higher magnification. The (1×1) overlay shows the registry of the clusters relative to the underlying substrate.

[12]. The STM image reveals this to be a low-density lattice gas of the cluster structures, with small domains of the $\sqrt{7}$ structure as well as isolated clusters.

Figure 1(d) is similar to Fig. 1(c), at higher magnification. A (1×1) atomic overlay is shown to determine the registry of the cluster structures relative to the underlying substrate. The Si adatoms, with local (2×2) or $c(2 \times 4)$ symmetry, are aligned with T_4 sites on the overlay (the $[11\bar{2}]$ direction was determined from a filled state (7×7) STM image on the same sample). All cluster structures center on a substitutional surface atom site, both in the case of isolated structures and for the little $\sqrt{7}$ domain outlined in the lower right. A similar analysis for isolated clusters adsorbed within (7×7) unit cells (not shown here) reaches the same conclusion: The clusters center on substitutional surface atom sites, suggesting a substitutional site for the metal atom at the center of the cluster.

To determine the structure in more detail we have performed MEIS studies, using shadowing and blocking. MEIS data were collected for 200 keV He^+ using beam doses of less than 10^{15} ions/cm². An ion scattered from Co on the surface can exit in any direction. However, if the Co is below the surface, the outgoing ion may be blocked by Si atoms. Thus, from the occurrence and directions of surface blocking minima the local bonding geometry can be determined with high accuracy [13]. Similarly, a subsurface Co atom may be shadowed from the incoming ion beam if the beam direction coincides with a Si-Co internuclear direction. In this paper we report the first observation of a metal blocking dip for a metal-semiconductor surface structure, from which the atomic structure is deduced. The absence of blocking dips in MEIS work on other systems allowed one to eliminate but not to deduce structural models [14,15].

In Fig. 2 we show the Co scattered intensity from the $\sqrt{7}$ structure in two different geometries. With the ion beam and detector rotated 6° out of the $(11\bar{2})$ scattering plane, no blocking minimum is observed (squares). Circles were measured in the $(11\bar{2})$ scattering plane, with the ion beam aligned with the $[\bar{3}11]$ channeling direction and the detector with the $[\bar{1}31]$ direction. Now, a clear blocking minimum is observed at 31.5° from the surface. This minimum immediately signifies blocking of Co by Si atoms, placing the Co-Si internuclear axis at an angle of 31.5° from the surface in each of the $\langle 110 \rangle$ azimuths, coincident with the orientation of the lobes in the STM empty states images. The width of the blocking minimum depends on the interatomic spacing. For larger Co-Si distance, the blocking dip is narrower. The width observed in Fig. 2 corresponds to a Co-Si spacing of about 2.3 Å. In addition, the scattered intensity outside the blocking minimum is reduced relative to the out-of-plane geometry, indicating shadowing along the incoming ion beam direction.

Based on the above observations we arrive at two possi-

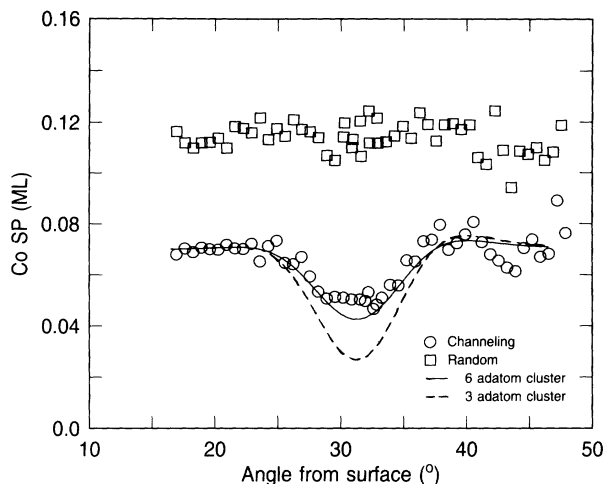


FIG. 2. Ion blocking profiles for Co atoms in the $\sqrt{7}$ surface show a blocking dip in the $[\bar{1}31]$ direction at 31.5° from the surface, with significant lowering at the shoulders due to shadowing (circles). By rotating the sample azimuth, an isotropic yield is observed (squares), free of shadowing and blocking. Calculated yields are shown for two candidate structures based on 3-adatom clusters (dashed line) and 6-adatom clusters (solid line).

ble unit cell structures, which we further reduce to one as described below. From the Co coverage required to saturate the surface with the $\sqrt{7}$ structure (0.12–0.14 ML), we know that there is one Co atom per unit cell. We also know that this Co atom is surrounded by at least three Si adatoms, one along each $\langle 110 \rangle$ azimuth at 31.5° above the cobalt. The STM images suggest that the Co atom occupies a substitutional site in the Si(111) surface. A schematic picture of a $\sqrt{7}$ arrangement of such 3-adatom structures is shown in Fig. 3(a). Assuming two orientational domains of 3-adatom clusters differing by 180° azimuthal angle, one type of domain would give rise to blocking without shadowing, the other type would give rise to shadowing without blocking. Alternatively, the structure may contain three additional Si atoms, as depicted in Fig. 3(b): Each Co atom is surrounded by six Si adatoms. In the 3-adatom structure, the Si adatoms are bridge bonded with two dangling bonds each. The addition of three more Si adatoms removes these dangling bonds, as well as three additional dangling bonds from the substrate, reducing the number of dangling bonds per unit cell from nine to three. Both shadowing and blocking now occur in each unit cell. Since the scattering from the two types of domains in structure 3(a) is independent, the absolute yield reduction due to shadowing is equal to the absolute yield reduction due to blocking (due to time-reversal symmetry of the ion trajectories). In structure 3(b), on the other hand, Co atoms that are already shadowed from the incoming beam are furthermore blocked on the outgoing path. Thus, the relative yield reduction due to shadowing

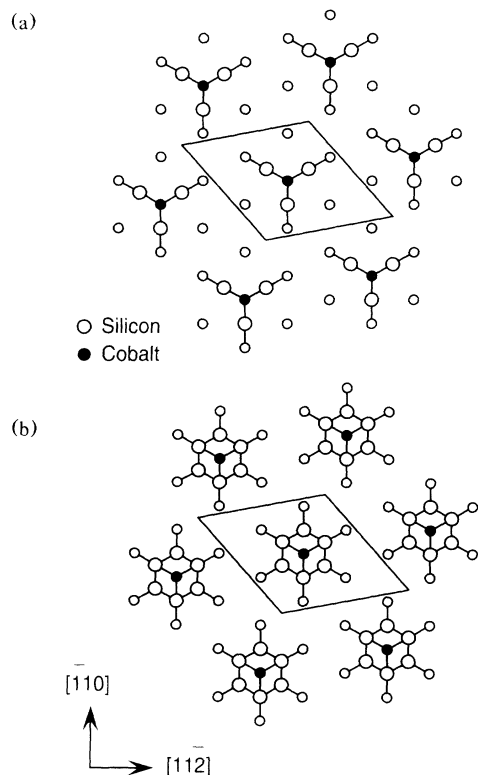


FIG. 3. Models for the $\sqrt{7}$ surface based on (a) 3-adatom clusters and (b) 6-adatom clusters. Ion scattering results support only the model with 6-adatom clusters.

should equal the relative yield reduction due to blocking. Inspection of the data reveals that the relative and not the absolute yield reductions are equal. To demonstrate this quantitatively, ion scattering simulations were performed for both structures. By varying the relative Si-Co vibrational amplitude the degree of shadowing (yield reduction outside the blocking dip) can be fitted for each model. The depth of the blocking minimum is then automatically determined and is not a free variable. We find that the 6-adatom model (solid line) is in excellent agreement with the data, while the 3-adatom model (dashed line) grossly overestimates the depth of the blocking minimum. We conclude that only the 6-adatom structure is consistent with the data.

We find an analogous blocking dip for the cobalt stabilized (1×1) surface with a cobalt coverage of 0.04 ML, showing that the local bonding configuration in the disordered structure is identical to that of the $\sqrt{7}$ structure. The latter is a crystallized version of the low-density (1×1) structure.

Intriguing features of the STM images may now be understood. The 6-adatom structure is threefold symmetric, with three fully coordinated "bridge adatoms" and three undercoordinated "cap adatoms." This symmetry is apparent in Fig. 1(a), where the three lobes in each unit cell derive from empty states on the cap adatoms. The single

lobes in the filled states image [Fig. 1(b)] appear to derive mainly from filled states on the Co atom. Recent calculations showing Co-derived filled surface states on the $\text{CoSi}_2(111)$ surface support this interpretation [16].

We note that the substrate allows two equivalent rotational orientations of the cluster. For clusters that are close packed in the $\sqrt{7}$ structure, a single orientation prevails, and the threefold symmetry is observed. On the other hand, clusters on the edge of a $\sqrt{7}$ domain, or entirely isolated, take on a ringlike appearance, with a weak sixfold symmetry. This may reflect a switching between the two orientations that is rapid on the time scale of the STM imaging process. This switch may be accomplished with only a small change of nuclear positions. Indeed, the MEIS data are best fitted by a superposition of two blocking dips 1.5° apart, one for each orientation of the 6-adatom cluster. This switching back and forth between two equivalent structures is similar to what is observed on the $\text{Si}(001)-(2 \times 1)$ surface [16]. It is also possible that the isolated 6-adatom cluster is actually sixfold symmetric, with a strong π -bonding component. In this description, the observed threefold symmetry of the close-packed clusters may result entirely from interactions between clusters.

The atomic arrangement determined for Co appears to be quite general for TM-silicon surfaces. Ringlike structures very similar to those in Fig. 1(c) have been observed on $\text{Si}(111)$ with Ni in the $(\sqrt{19} \times \sqrt{19})$ structure [8], and for very low Pd coverages [17]. Such structures are often inadvertently produced through trace metal contamination [18]. The image of the (1×1) structure presented in Fig. 1(c) shows both the severe disorder and the atomic origins of impurity stabilized $\text{Si}(111)-(1 \times 1)$ surfaces. It is seen that transition-metal adsorbates can inhibit long-range ordering of surface structures at a coverage below the detection threshold for many techniques.

We note that the local environment of cobalt in the $\text{Si}(111)-(\sqrt{7} \times \sqrt{7})\text{Co}$ structure is similar to that in bulk and interface silicide structures [19-21]. The six silicon neighbors to cobalt in the $\sqrt{7}$ structure comprise a Si-M-Si triple layer with 2.3 Å bond length, similar to bulk CoSi_2 . In the $\sqrt{7}$ structure the coordination of the metal atom is only 6 (instead of 8 in CoSi_2), however, this may be compensated by back-bonding charge from the three capping adatoms in the cluster, since they carry dangling bonds. In this sense, the $\sqrt{7}$ structure may be viewed as an intermediate structure between the clean surface and the fully developed $\text{Si}(111)/\text{CoSi}_2$ interface, and already exhibits many features of the latter.

We gratefully acknowledge useful discussions with J. Demuth and J. Tersoff. A portion of this work (P.A.B.) was supported by NSF Grant No. DMR8921124.

(a)Present address: 185A-Coordinate Science Laboratory,

- University of Illinois, Urbana, IL 61801.
- [1] M. A. Nicolet and S. S. Lau, in *VLSI Microstructure Science*, edited by N. G. Einspruch and G. B. Larrabee (Academic, New York, 1983), p. 330.
- [2] K. N. Tu and J. W. Mayer, in *Thin Films—Interdiffusion and Reactions*, edited by J. M. Poate, K. N. Tu, and J. W. Mayer (Wiley, New York, 1978), p. 359.
- [3] R. T. Tung, Phys. Rev. Lett. **52**, 461 (1984).
- [4] J. Tersoff and D. R. Hamann, Phys. Rev. B **28**, 1168 (1983).
- [5] C. Calandra, O. Bisi, and G. Ottaviani, Surf. Sci. Rep. **4**, 271 (1985).
- [6] P. J. van den Hoek, W. Ravenek, and E. J. Bacrends, Phys. Rev. Lett. **60**, 1743 (1988).
- [7] D. D. Chambliss and T. N. Rhodin, Phys. Rev. B **42**, 1674 (1990).
- [8] R. J. Wilson and S. Chiang, Phys. Rev. Lett. **58**, 2575 (1987).
- [9] K. Akiyama, K. Takayanagi, and Y. Tanishiro, Surf. Sci. **205**, 177 (1988).
- [10] L. J. Chen, H. C. Cheng, and W. T. Lin, in *Thin Films—Interfaces and Phenomena*, edited by R. J. Nemanich, P. S. Ho, and S. S. Lau, MRS Symposia Proceedings Vol. 54 (Materials Research Society, Pittsburgh, 1986), p. 245.
- [11] P. A. Bennett, M. Copel, D. Cahill, J. Falta, and R. M. Tromp, in Proceedings of the Thirty-Seventh AVS Meeting, Seattle, Washington, 1991 (to be published).
- [12] J. V. Florio and W. D. Robertson, Surf. Sci. **24**, 173 (1971).
- [13] J. F. van der Veen, Surf. Sci. Rep. **5**, 199 (1985).
- [14] M. Copel and R. M. Tromp, Phys. Rev. B **39**, 12688 (1989).
- [15] M. Chester and T. Gustafsson, Phys. Rev. B **42**, 9233 (1990).
- [16] K. W. Sulston and S. M. Bose, J. Phys. Condens. Matter **3**, 7607 (1991).
- [17] U. K. Koehler and J. E. Demuth (private communication).
- [18] Private communication from numerous experimentalists who prefer to remain anonymous.
- [19] D. R. Hamann, Phys. Rev. Lett. **60**, 313 (1988).
- [20] I. K. Robinson, R. T. Tung, and R. Feidenhans'l, Phys. Rev. B **38**, 3632 (1988).
- [21] E. J. van Loenen, J. W. M. Frenken, and J. F. van der Veen, Phys. Rev. Lett. **54**, 827 (1985).

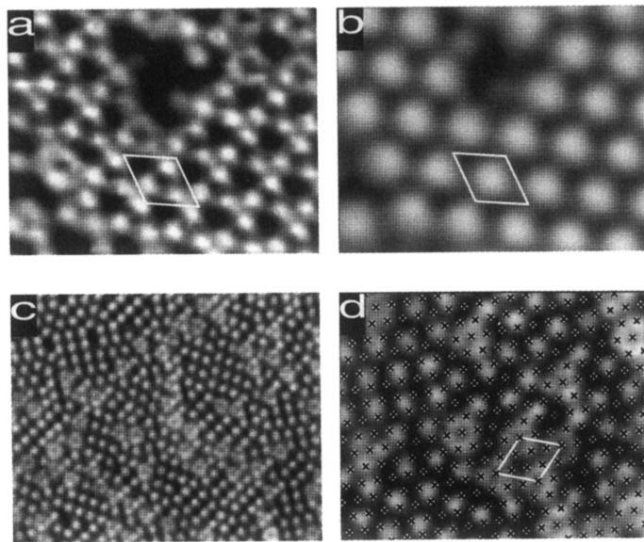


FIG. 1. STM images of Co adsorbed on Si(111). (a) Empty states image (+2.0 V) of the $\sqrt{7}$ surface with a single unit cell outlined. Trimer lobes point in $\langle 110 \rangle$ azimuths. (b) Matching filled states image (-1.8 V). (c) Empty states image (+2.2 V) of the (cobalt) “impurity stabilized 1×1 ” surface. It is a lattice gas of the clusters coexisting with silicon adatoms. (d) Like (c), at higher magnification. The (1×1) overlay shows the registry of the clusters relative to the underlying substrate.