Interstitial Precursor to Silicide Formation on Si(111)-(7 × 7)

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We show that cobalt atoms deposited on Si(111)-(7×7) at room temperature occupy near-surface interstitial sites of the silicon lattice at very low coverages. These sites are visible in scanning tunneling microscopy images as slightly lowered groups of 2 or 3 adjacent Si adatoms in an otherwise intact Si(111)-(7×7) surface. At 150°C the interstitials are mobile and preferentially occupy sites directly under 3-coordinated silicon surface atoms ("rest atoms") on the faulted side of the 7×7 unit cell. An atom-displacing silicide reaction occurs only for higher coverages, when 7×7 half-unit cells become multipy occupied.

The initial stages of reaction for transition metals (TM) deposited on a silicon surface is a widely studied topic with both practical and fundamental motivations. 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]. Fundamental challenges remain, however, since little is known on the atomic scale about the structure and kinetics in the initial stages of the reaction.

Regarding structure, it is known from a wide variety of experiments that a silicide reaction occurs "spontaneously" upon deposition of most TM's at room temperature up to about 15 Å at which point the reaction stops due to island coalescence and diffusion limitations, as exemplified in the Ni/Si system [2]. Yet the identity and prediction of the "first phase" (among several possible stoichiometries) formed remains controversial [3]. Most techniques, such as ion scattering, Auger, reflection high energy electron diffraction, and photoemission lack structural sensitivity on the coverage scale ($\ll 1$ monolayer) where metal atoms on average are well separated, i.e., the true *initial* stage of the reaction.

Regarding kinetics, it has been questioned how a reaction can occur at all beyond the first layer, since this requires breaking Si-Si bonds and significant mass transport [4-6]. Hiraki proposed that Si-Si bonds are weakened by a metallic overlayer that forms after a critical thickness of several monolayers (ML) [4]. Tu proposed that a high concentration of metal interstitials in silicon could promote liberation of silicon, interdiffusion, and reaction [5].

In this Letter we show that the silicide reaction in a model metal-semiconductor system, Co/Si(111), is preceded by a metastable state consisting of metal atoms in silicon interstitial sites just below the surface. This state occurs at room temperature and very low coverage where individual reaction sites can be seen directly in scanning tunneling microscopy (STM) images. The behavior of this interstitial precursor state in the nucleation and early growth of the silicide can strongly affect the structure of thicker, reacted overlayers.

The STM instrument used for these studies features a dual level approach with "stabilizing foot" and tripod scanner. Samples were prepared from 0.1 Ω cm As doped wafers rinsed in methanol, degassed at 1000 K, and flashed to 1450 K. Metal was deposited from a miniature electron bombardment evaporator at a rate of 0.19 ± 0.02 ML/min (1 ML $= 7.83 \times 10^{14}$ Co atoms/cm^2). Very small coverages of 0.01 ML were specifically calibrated by *ex situ* ion scattering measurements on an accumulation of 20 identical doses.

In order to describe the data, we first show in Fig. 1 the accepted dimer–adatom–stacking-fault (DAS) model structure for the clean Si(111)-(7×7) structure [7].

In Fig. 2 we present STM topographic images showing the coverage dependence of structures formed for deposition at 25°C [panels (a)-(d)] and at 150°C [panels (e) and (f)]. At a coverage of ~0.81 ML [panel (d)], we see island features approximately 20 Å wide and 2.0 Å high. There is no sign of the original 7×7 structure. Of course, the composition of these islands cannot be determined using STM; however, ion scattering measurements at somewhat higher coverage suggest these are reacted silicide islands [8]. For a coverage of 0.18 ML [panel (c)], we see atomic scale features suggestive of displaced Si or Co atoms. Remnants of the original 7×7 are apparent: One can identify most of the corner holes and some of the adatoms. There is no difference in reactivity (at this temperature) between the faulted and unfaulted halves of the 7×7 unit cell. For a coverage of ~0.014 ML [panels (a) and (e)], we see a nearly perfect 7×7 surface. There are no extra features and all adatoms are visible in their correct lateral positions. The pattern of heights of the adatoms is characteristic of clean Si(111)-(7×7): The 6
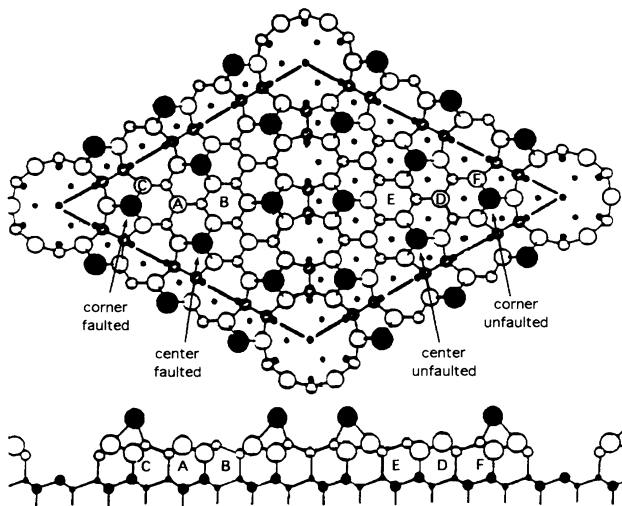
FIG. 1. DAS model for Si(111)-(7×7). The left (faulted) half of the unit cell has a wurtzite stacking of the top bilayer. 12 silicon adatoms sit on filled threefold (T_4) sites of the surface bilayer and are distinguished as center vs corner adatoms (3 each of 4 types per unit cell), as shown. Locations of the near-surface interstitial sites types A-F are shown.
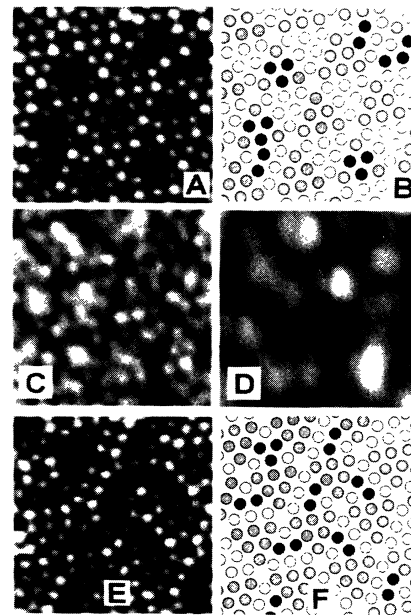

FIG. 2. STM filled states topographic images (-1.4 V, 0.4 nA, 75 Å edge) of cobalt deposited on Si(111) at room temperature for coverages of 0.016 ML (a), 0.18 ML (c), and 0.81 ML (d) and at 150°C for coverage of 0.012 ML (e). The locations of dimmed adatoms in (a) and (e) are marked in (b) and (f). Each image shows a different region of the surface.

adatoms on the faulted side of each unit cell appear higher than the 6 on the unfaulted side, and the 3 corner adatoms appear higher than the 3 center adatoms in each half of the unit cell [9]. On closer inspection, we find that a few of the adatoms [as marked in panels (b) and (f)] appear dimmer in the grey scale rendition of tip height than their symmetry equivalents, showing an apparent lowering of ~0.9 Å with 1.4 V bias. The dimming is enhanced at smaller negative sample bias, while the lateral resolution becomes worse. No height contrast at all is observed at positive sample bias, in the explored range of 0–3 V. These observations show that the first Co atoms deposited on the surface do not significantly move any Si atoms, unlike the case at higher coverage.

The dimmed adatoms occur in definite groups. They are mostly center adatoms and mostly occur as equally dimmed pairs or triplets on a given half of the 7×7 unit cell. The corner adatom nearest a given pair is also slightly dimmed. Occasionally a corner adatom is strongly dimmed [upper right of panel (a)]. The center adatoms adjacent to it typically have one dimmer and one brighter than their symmetry equivalents in nearby unit cells. In this particular example, it appears that a pair of center adatoms is also affected. Overall, we identify 6 different types of reaction sites which we call faulted pair (type A), faulted triplet (type B), faulted corner (type C), unfaulted pair (D), unfaulted triplet (type E), and unfaulted corner (type F). Contamination related defects are also seen occasionally. They are readily distinguished from the reaction sites by their appearance as very low or "missing" adatoms with strong contrast at all bias voltages with ±3 V.

This distribution of reaction sites is not random but

shows trends as summarized in Fig. 3 where we show the "site population," defined as the number of occupied sites of each type normalized to the total number of occupied sites. Overall coverage is 0.016 and 0.012 ML for 25 and 150°C, respectively. The error bars represent 1 standard deviation due to counting statistics. If the sites were randomly occupied, their populations would reflect their degeneracies, which are 3, 1, and 6 for pair (type A and D), triplet (type B and E), and corner sites (type C and F), respectively. This clearly does not occur, either for cold or warm deposition. For example, at 25°C, there is a clear avoidance of corner sites on the faulted site (type C), and avoidance of pair sites on the unfaulted side (type D). On the other hand, if we count sites of all types, the total populations on the faulted side (sum of types A, B, and C) vs unfaulted side (sum of types D, E, and F) *are* statistically equal at 25°C but distinctly unequal at 150°C where a strong preference for the faulted side is observed. Implications of these results are discussed later.

On the strength of the following arguments, we have determined that each type of reaction site contains a single cobalt atom. First, we find that the total number of sites observed is closely equal to the number of cobalt atoms deposited per unit area. For example, in an area of 6.4×10^4 Å^2 we count 81 reacted sites, while the average number of metal atoms deposited in this area is 80. These agree within the uncertainty of counting statistics and dose calibration (about 15% each). If the triplet and
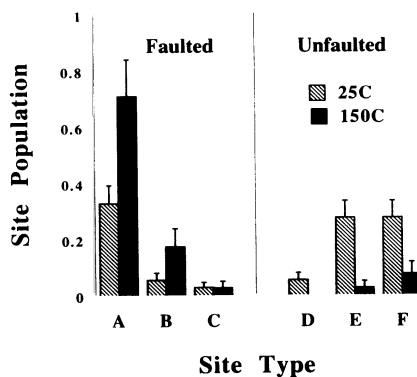
FIG. 3. Site populations (number of occupied sites of each type normalized to the total number of occupied sites) for deposition temperatures of 25 and 150 °C. Error bars show 1 standard deviation due to counting statistics. Degeneracies of the sites (number per unit cell) are 3, 1, and 6 for pair (types A and D), triplet (types B and E), and corner sites (types C and F), respectively.

pair sites contained 3 and 2 metal atoms each, the total number of metal atoms in the area would be 227, clearly outside the uncertainty. Second, we note that the site populations are not consistent with having clusters of metal atoms in each site. For example, assuming random adsorption and essentially zero mobility, the cluster populations would be approximately (f), $(f)^2$, and $(f)^3$ for singlet, pair, and triplet groups, respectively, where (f) is the number of metal atoms per half-unit cell of 7×7. This is inconsistent with the experiment, which shows, for example, more triplets than pairs on the faulted side (sites E vs D) and no singlets at all on either side. Third, the distribution of sites is independent of total coverage in the measured range from 0.003 to 0.016 ML. Based on these observations, we conclude that indeed *each reaction site contains a single metal atom.*

It is expected that reaction sites as defined above will overlap at higher coverage. The probability that a given reaction site overlaps a second reaction site on the same half-unit cell is given approximately by f^2, assuming random adsorption. For a coverage of 0.016 ML [as in Fig. 2(a)] we have $f = 0.4$ and $f^2 = 0.16$. However, no clearly identifiable overlapped sites are seen. In particular, we exclude the possibility that triplet sites are overlapped pairs, based on their relative populations and based on the threefold symmetry of images of the triplet site. The low symmetry of images of the corner sites [type F is shown in Fig. 2(a)] suggests they may be such overlapped sites, yet their population is lower than expected for a random adsorption process. Apparently there is a net repulsive interaction between reaction sites and a finite mobility even at 25 °C such that site overlap is suppressed.

Next we discuss the atomic geometry of the reaction sites. The metal atom cannot be "on" the surface [such as in the Ag/Si(111) system [10]] since it would then appear with high contrast at some bias voltage in the ± 3 V

range we searched. Calculations for $CoSi_2$ show a large density of both empty and filled states with s-p-d hybridized orbitals near the Fermi level [11]. In any case, the relatively low coordination of surface adsorption sites make them an implausible location for transition metals, which bond with 6 or more neighbors in bulk silicide compounds [1]. Since no silicon atoms in the reaction site are significantly moved, we conclude that the metal atoms are below the surface in silicon interstitial sites. The dimming of silicon adatoms in the STM filled states images is presumably due to a transfer of charge out of the p_z orbitals of the adatoms into the adatom backbonds and nearby rest atoms of the 7×7 structure. This process is known to occur on the clean 7×7 surface (indeed it generates the adatom height contrast) [9] and is apparently enhanced in this case by the presence of metal atoms just below the surface. We can then specify the lateral positions of metal atoms based on the symmetry of the STM image. Since the adatoms in each pair or triplet group (types A, B, D, or E) are dimmed equally, we infer that the metal atom is equidistant from them. Thus is lies on the midplane between a pair group, or on the line centered on the triplet group of adatoms. The lateral positions can then be uniquely assigned as shown in Fig. 1. For the lower symmetry corner adatom groups (C and F) the sites are assigned between the corner and center adatoms, closer to 1 center adatom.

From the behavior of the site populations we can infer characteristics of the mobility and energetics of the interstitials. At room temperature, they are completely immobile, since their locations are unchanged in images taken 5 min apart. On the other hand, we infer a nonzero mobility during the deposition process, since the metal atoms arriving at random locations on the surface manage to reach the preferred pair or triplet site on a given half of the unit cell, implying a "diffusion length" on the order of the adatom spacing, 7 Å. At the same time, this diffusion length must be less than the 7×7 unit cell length, 27 Å, since the diffusing metal atoms remain on the half of the unit cell they strike on arrival, populating the halves equally. This transient mobility or athermal diffusion may be due to the heat of adsorption of the arriving metal atoms. We note that the diffusivity for transition metal interstitials in bulk silicon is very high: They would travel the unit cell length of 27 Å in 0.1 sec at room temperature [12]. Thus, the mobility of the interstitials observed in the surface region is orders of magnitude lower than in the bulk.

At 150 °C deposition temperature, we infer that the diffusion length during the 10 sec required for dosing and quenching is larger than the 7×7 unit cell length, 27 Å, since the diffusing metal atoms can reach the preferred half of the unit cell, populating the halves unequally. Given that the interstitials are mobile at this temperature, it is perhaps surprising that they do not diffuse deep into the bulk and disappear from the STM image. This is prevented by the low bulk solubility of $\sim 10^{-10}$ ML/

wafer at this temperature [12].

We can rank the relative binding energies for the sites if we assume their occupancy factors at 150 °C reflect a thermally equilibrated population. Thus the binding energies for sites A and B are nearly equal (since their populations follow their degeneracies), and are distinctly larger than for all other sites. This result is rather surprising. On the basis of bonding geometry, one would expect the energy of metal atoms on the A and D sites to be similar since they each have a surface dangling bond for a near neighbor. Hamann and Mattheiss have shown in a related calculation that the surface dangling bond lowers the total energy for Ni interstitials below a Si(111)-(1×1) surface by 0.6 eV [13]. From our experiments, it appears that the energetics of the near-surface interstitials are determined by subtleties of long-range charge transfer and/or wave function symmetry rather than simple coordination arguments. Thus, the strong preference for the faulted side of the 7×7 unit cell regardless of local coordination may be simply due to the enhanced density of occupied states near the Fermi level on the faulted side [10].

From our experiments a new picture of the silicide reaction at low temperature emerges. The first metal atoms deposited on a Si(111) surface exist metastably as near-surface interstitials [14–16]. They can reach an atomic concentration $c \sim 10^{-2}$, which is remarkably high compared with the maximum bulk solubility of $c \sim 10^{-6}$ [12]. On the other hand, it is known from total energy calculations that stoichiometric concentrations $(c \sim 1)$ of interstitials are energetically unstable to silicide formation [13]. What then is the nature of the "transition" from interstitial precursor to silicide compound? Our experiments suggest that this occurs at a *nominal* coverage of ~ 0.04 ML, where all half-unit cells of 7×7 are occupied. The next metal atoms to arrive must then interact with existing interstitials. We speculate that this forms the nucleus for an atom-displacing silicide reaction. This of course is a highly localized event not well described by equilibrium models [4,17]. The nucleation behavior will vary with temperature. At low temperatures the nucleation density will be high due to statistical overlap of interstitials that essentially remain where they land on the surface, while higher temperatures will favor a more dispersed, equilibrium population of interstitials which will suppress nucleation. Regardless of the specific reaction mechanism, we note that the path of the reaction is determined by the interstitial precursor, not the metal-silicon compound that forms at higher coverage. Thus, for example, the larger binding energy we find for interstitials on the faulted side of the 7×7 unit cell readily explains the fact that reacted islands form first on the faulted side of Si(111)-(7×7) for several metals, including Co, Pd, and Ag [10,16,18].

It is likely that other transition metals will behave similarly to cobalt, and possible that Si(100) will also support interstitials. It has been suggested elsewhere that metal interstitials play an important role in reactions at buried interfaces [5], and may affect or control the Schottky barrier height at silicide-silicon interfaces [19]. Unfortunately, their presence and influence at buried interfaces is difficult to quantify [20]. Thus, the capability demonstrated here of imaging individual near-surface interstitials with STM should encourage further studies of this important topic.

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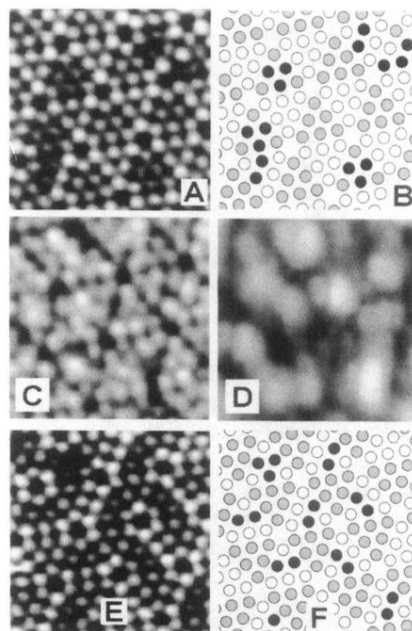
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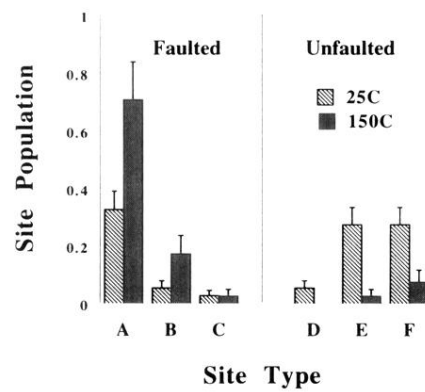
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