Hydrogen termination following Cu deposition on Si(001)

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We describe the surface structures following submonolayer Cu deposition on Si(001) and subsequent hydrogen termination as characterized by scanning tunneling microscopy. Cu adsorption at 870 K results in a characteristic (2×8) island+vacancy structure, as previously reported. In addition, occasional structures are observed attributed to Cu in surface interstitial sites. After H termination, the dominant features of the island+vacancy structure remain, but the size and distribution of the structures are significantly altered. Based on the atomic-scale appearance of both the clean and H-terminated structures, we propose that within the (2×8) island+vacancy structure all surface atoms are Si, with all Cu subsurface, contrary to previous structural models.

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The deposition and surface chemistry of metals on silicon is of considerable importance both to current technology and emerging nanoscience. Technologically, the Cu—Si(001) interface is of particular significance, with current integrated circuit technology incorporating Cu interconnects formed by techniques such as ion-assisted trench filling.[1] Although Cu is a key component of such interconnects, interdiffusion of Cu from the surface into the bulk of the silicon chip can adversely affect device performance.[2] Therefore, a further understanding of the Cu/Si interface, Cu contamination in Si, and the potential effects of hydrogen—ubiquitous in processing—could be significant in combating surface-to-bulk diffusion of Cu on Si and in improving the processing of valuable Cu-based interconnects.

In addition to the importance of metal-Si interactions in current device technologies, such interactions are fundamentally important in the design of nanostructured surfaces. Transition metals, such as Co, Ni, and Cu, are known to react readily with Si to form metal silicides.[3] In the case of Ni, this reactivity has been exploited to create templates for metal deposition with nanometer scale order.[4] In the case of Cu, the high diffusion[5] and reactivity of Cu in Si make this system an intriguing candidate for the construction of similar nanoscale structures. The surface reactivity and stability can be further modulated by chemically functionalizing the surface. For example, hydrogen termination of Si is particularly well understood, both for manipulating the surface chemistry and clarifying the surface structure.[6]

The deposition and growth of Cu on Si has been studied previously by a variety of techniques.[7–11] Scanning tunneling microscopy (STM) has been especially useful in exploring the Cu/Si surface on different crystal faces.[12–17] On the clean Si(001) surface, STM studies by Ichinokawa and co-workers,[16–18] Lindsay and co-workers,[12] and Nogami and co-workers[14] have all shown that the deposition of Cu results in the formation of islands and vacancies. The location of Cu on these surfaces, however, has yet to be resolved.

Herein we report an STM analysis of the initial growth of Cu on Si(001) and the effects of subsequent hydrogen termination on the Cu-induced surface structure. Hydrogen termination causes numerous changes in the surface structure, some of which strongly suggest that previous structures proposed for Cu/Si(001) are incorrect. To our knowledge, this work presents the first report of the effects of hydrogen following submonolayer metal depostion on Si(001).

Experiments were performed in ultrahigh vacuum (UHV) (base pressure $\sim5\times10^{-11}$ Torr) using Sb-doped Si(001) wafers (0.01–0.02 Ω cm) oriented to within 0.1° of (001). Samples were initially degassed in UHV overnight. Clean surfaces were prepared by resistively heating for 30 s at 1500 K, cooling for at least 5 min, and then briefly heating again to 1500 K for 5 s. The heating power was then reduced until the sample temperature desired for deposition was reached. Sample temperatures were determined from the heating power as described previously.[19]

Copper was evaporated from a pure Cu wire wrapped in a resistively heated W wire. Samples were held at 870 K during Cu deposition to reproduce the highest deposition temperature previously reported.[14,15] In order to mimic the exposure conditions to be used during H termination, after depositing Cu the sample was post annealed in UHV for 10 min at 615 K. A total coverage of ~0.6 to 1.25 ML of Cu ($1\ \mathrm{ML}=6.78\times10^{14}\ \mathrm{cm}^{-2}$) was deposited at a rate of $0.6\ \mathrm{ML\ min}^{-1}$ as measured with a quartz crystal microbalance. It is important to note that our substrate deposition temperature is at the high end of those reported previously (720–873 K),[14–16,18] which increases Cu diffusion into the bulk, lowering the effective Cu coverages on our surfaces compared to those dosed at lower substrate temperatures.

To terminate a surface with H, a sample was held at 615 K and exposed for 2 min to atomic H produced by a hot tungsten filament (located ~1 cm away from the sample) and a background H_2 pressure of 1×10^{-5} Torr. After H exposure, each sample was annealed again in UHV for 10 min at 615 K. On clean surfaces etching is not observed under these conditions.[20] All STM images were collected at room temperature starting ~1 h after preparing the surface. All results shown are filled-state, gray-scale images collected at 2–3 V with constant currents of 0.1–1 nA.

A typical STM image of Cu (~1.2 ML) deposited at 870 K on clean Si(001) is shown in Fig. 1, where a large number of islands (bright protrusions) and vacancies (dark recesses) are observed. At higher Cu coverage an overall $c(8\times8)$ reconstruction occurs.[14] The atomic-scale structure of the island+vacancy structure observed at low coverage is shown in Fig. 1(b), where a dashed box highlights one (2×8) unit cell. The islands are always oriented normal to the direction of the dimer rows and typically consist of three

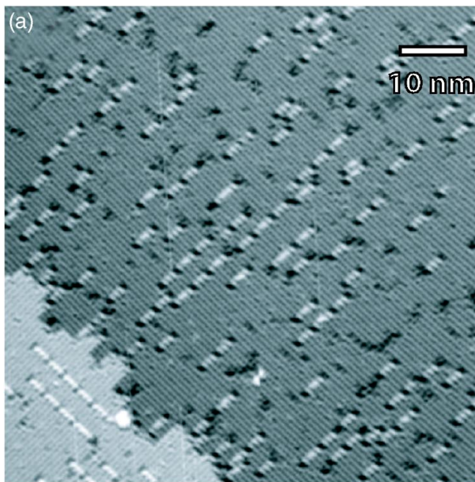
protrusions, each centered on a dimer row. Dimer vacancies, one of which is labeled *DVVVVD* in Fig. 1(b), are observed between and at the end of the islands.

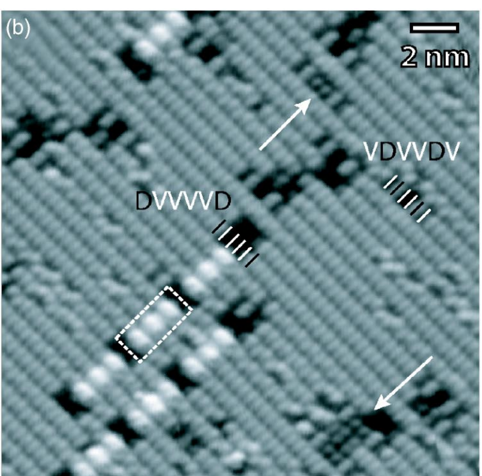
Previously proposed structural models have assumed that these vacancies consist of two missing dimers.[12,14] Our atomic resolution images clearly show that these vacancies actually include *four* missing dimers, invalidating all previous structural models. We believe this discrepancy is a consequence of image resolution; a dull tip can make islands seem wider and make vacancies seem smaller than actual. In addition, longer islands with more than three bright features are occasionally (but rarely) observed, forming $(2\times n)$ features. In these $2\times n$ islands, additional bright protrusions reside between the dimer rows (not shown).

Additional vacancies observed on the surface after Cu deposition are very similar to the ones observed on clean Si(001). An analysis of the observed vacancy type and frequency, along with a comparison of the dimer vacancies observed on clean Si(001) from Wang *et al.*[21] is presented in Table I. Interestingly, one specific pattern is observed with high frequency on our Cu/Si(001) surfaces, an example of which is labeled *VDVVDV* on the right side of Fig. 1(b). The pattern consists of a vacancy, a dimer, two vacancies, a dimer and a vacancy. After Cu deposition this pattern is observed ~30 times more frequently than on the clean surface, indicating it is a Cu induced structure. Transition metal incorporation in the silicon surface often leads to distinctive dimer vacancy complex formations. A classic example is the case of Ni on Si(001), in which concentrations of as little as 5% create arrays of line vacancies.[22,23]

We observe an unusual structure on this surface that does not appear to have been noted in the past. Two examples are highlighted with arrows in Fig. 1(b), and the general structure can be determined from Fig. 1(c). The new structure consists of two round protrusions centered in the middle of the dimer row, with each protrusion offset from the dimer position by half a dimer. Note that copper impurities in bulk Si reside either at substitutional or interstitial sites. It is reasonable to assume that substitutional Cu will produce features aligned with the Si lattice. In contrast, the unusual location of these protrusions with respect to the lattice suggests they are interstitial Cu atoms at the surface.

The effects that H termination has on the Cu/Si(100) island+vacancy surface are shown in Fig. 2. There are several apparent differences produced by the hydrogen termination. First, the average island length increased. Whereas islands on the Cu/Si(001) surface preferentially consist of three bright maxima and a terminating vacancy on each end, after hydrogen termination longer islands are observed (Fig. 3). Another difference is the position of the vacancies with respect to the islands—the islands are no longer preferentially terminated by vacancies. On average, one terminating vacancy of every island appears to have diffused away from the island. The remaining vacancies show no recurring pattern, randomly occurring as on a clean surface. Figure 2(b) shows two common island+vacancy structures observed after hydrogen termination. Qualitatively, the islands look strikingly similar to Si islands created during Si homoepitaxy, where islands composed of 5–9 consecutive dimers are often observed. On the atomic scale, all features are identical





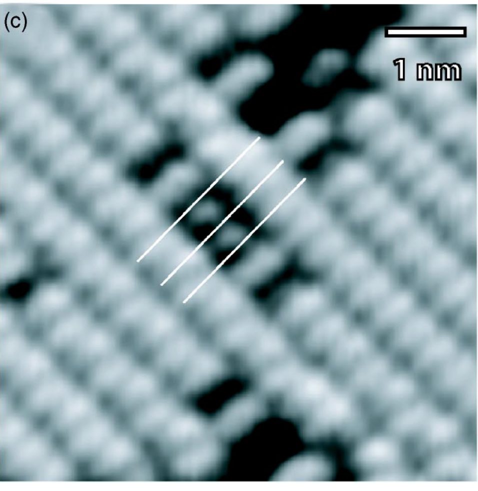


FIG. 1. (a) Filled-state STM image of ~1.2 ML Cu deposited on Si(001) at 870 K. (b) The dashed box highlights a (2×8) unit cell. A four dimer-long terminating vacancy is labeled *DVVVVD*, and a frequently observed defect structure is labeled *VDVVDV*. The arrows point to features attributed to interstitial Cu atoms. (c) High-resolution image of two proposed interstitial Cu atoms. The lines highlight the location of adjacent dimers.

to the symmetric dimers observed on monohydride-terminated Si(001), including the underlying structures within the vacancy islands.

TABLE I. Notation, pattern, and observation of dimer vacancy defects from Ref. 21, and this study. The fraction n is the ratio of the number of defects N to the total number of observed dimers.

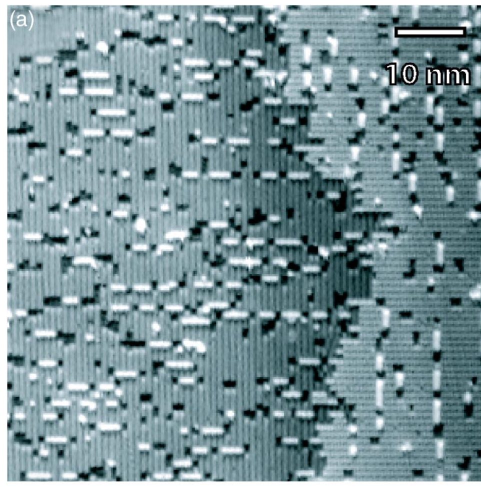
	Clean Si(001)		Cu on Si(001)[a]	
Dimer notation and pattern	number of defects N	Fraction n (10^{-3})	number of defects N	Fraction n (10^{-4})
V	148	6.7	55	11.5
VV	78	3.5	6	1.3
VDVV	244	11.0	11	2.3
VDVVDV	6	0.3	40	8.3
VVV	23	1.0	8	1.7
VVVDV	54	2.5	2	0.4
VDVVVDV	100	4.5	2	0.4
VVVV	0	0.0	7	1.5

[a]Does not include vacancies associated with islands.

Previous reports of Cu deposition on Si(001) are somewhat inconsistent. Ichinokawa and co-workers proposed a Cu/Si(001) phase diagram with mixed (2×1), (2×2), (6×2), and $c(12\times10)$ phases for 0.1–20 ML Cu coverage and 670–870 K substrate temperatures. In the interpretation of their STM results, the bright islands observed at low coverage (0.1 ML) were attributed to Si ejected from a dimer row by the deposition of Cu, which they proposed to be bound under the island. In contrast, STM studies by both Nogami and co-workers and Lindsay and co-workers reported only a $c(8\times8)$ phase. Lindsay and co-workers attributed the presence of a $c(8\times8)$ phase on Si(001) to Cu contamination, as identified by secondary ion mass spectrometry. No structural model was ever proposed for the actual position of the Cu contaminants on the reconstructed surface. Nogami and coworkers, who deposited submonolayer ($\sim$0.05–0.20 ML) Cu on Si(001) at 720–870 K, proposed a structural model with Cu residing at the island maxima and a two dimer vacancy, in contradiction to the ejected Si model of Ichinokawa and co-workers.

We observed a $c(8\times8)$ surface similar to the one reported previously by Nogami and Lindsay, but believe that Nogami's model is incorrect. Copper normally occupies an interstitial site when present in bulk Si; however, theoretical simulations have shown there is a significant energetic advantage (2.71 eV) for interstitial Cu^{+} to react with Si vacancies and form substitutional Cu.[24] Therefore, it is probable that Cu initially goes in the surface interstitially, and then reacts through surface defects to occupy substitutional sites, ejecting Si atoms in the process which then become the observed homoepitaxial-like islands. This mechanisms is further supported by reports that Si deposition onto defect-rich surfaces results in similar island structures.[25]

Ab initio calculations by Estreicher show that the Cu-Si bond is less stable than the Si-H bond by approximately 2 eV.[26] Therefore, H passivation should have a significant effect on any Cu present at the surface. If the islands were made out of Cu, as suggested by Nogami, one would expect



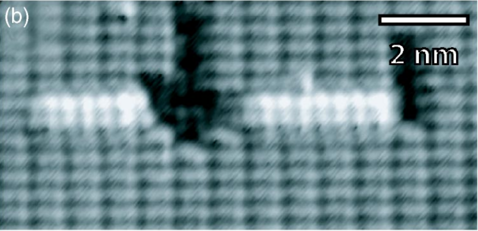


FIG. 2. Filled-state STM images of $\sim$1.2 ML Cu deposited on Si(001) at 870 K, followed by H termination at 615 K. (b) The atomic-scale structure of a typical island.

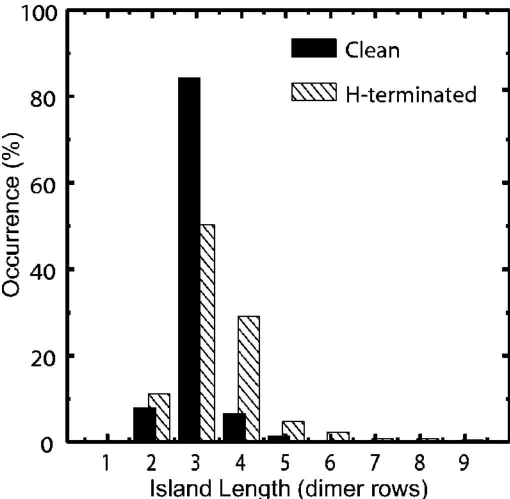


FIG. 3. Distribution of island lengths (relative to dimer row width, 0.768 nm) on Si(001) following Cu deposition (filled bars) and after subsequent hydrogen termination (dashed bars).

hydrogen termination to displace the Cu from the surface and therefore reduce or eliminate the islands. Although STM cannot unambiguously determine the position of Cu in the reconstruction, in light of the images obtained following hydrogen termination, where only H-terminated Si-like features are observed, we propose that all Cu is subsurface after H termination. We believe the results to date are best explained by a model where each Cu atom initially enters the Si lattice interstitially, then ejects a Si atom from the lattice to occupy a substitutional site either underneath a Si island or an adjacent vacancy. After H passivation, which changes the surface energies, surface Si atoms no longer bond to the Cu, driving the Cu into the bulk and allowing the islands and vacancies to reconstruct into the structures observed.

Our essential structural results can be seen in composite in Fig. 4. Clean Si(001) exposed to Cu has a distinct island +vacancy structure [which becomes a $c(8\times8)$ reconstruction at high coverage]. We propose that Cu enters the surface at interstitial sites and relaxes into substitutional sites ejecting Si atoms in the process. Most of the near-surface Cu is underneath the Si islands and within the vacancies, with the remaining residual in interstitial sites. When the Cu/Si(001) surface is hydrogen terminated, the island+vacancy structure is retained but the size and distribution of the structures are altered. This change is in contrast to monohydride-terminated Si(001), where surfaces with extremely low defect densities are routinely achieved. Based on the atomic-scale appearance of the H-terminated Cu/Si(001), we propose that all surface atoms are H-terminated Si, and that all Cu is actually subsurface. Note that such a surface structure—Si(001):H with a relatively narrow distribution of defects—could make an interesting template for nucleating nanostructures. We are presently investigating how these defects affect the subsequent nucleation and growth of metal monolayers.

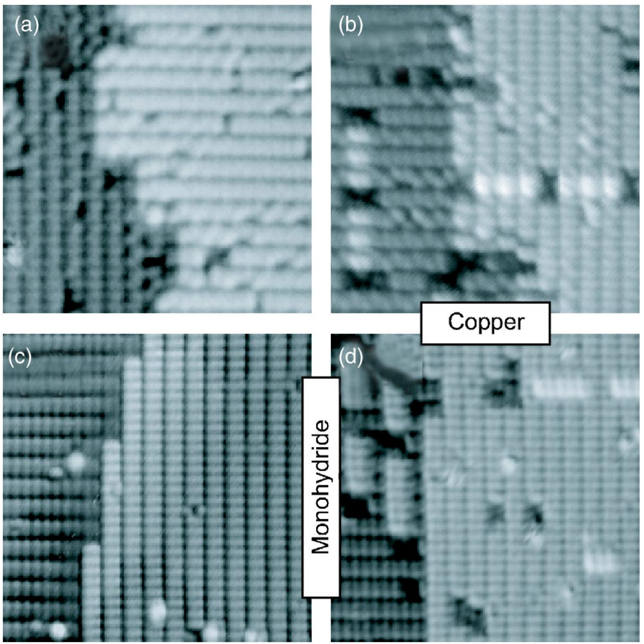


FIG. 4. Composite of the surface structures observed in this study. (a) Clean Si(001), (b) Cu-dosed Si(001), (c) hydrogen-terminated Si(001), (d) hydrogen-terminated, Cu-dosed Si(001).

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