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Quantitative analysis of Si mass transport during formation of Cu/Si(111)-(5×5) from scanning tunneling microscopy

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The Si mass transport taking place during the formation of the Cu/Si(111)-(5×5) surface phase has been studied using scanning tunneling microscopy. From the measurement of the areas occupied by various structural domains and the quantitative consideration of the Si mass balance, the top Si atom density in the Cu/Si(111)-(5×5) phase is found to be 0.96 monolayer. The Cu/Si(111)-(5×5) structure is suggested to consist of a planar CuSi overlayer with an atomic ratio of Cu:Si close to 1:1. Further Cu deposition beyond the formation of Cu/Si(111)-(5×5) phase results in the formation of Cu nanocrystals on the intermediate (5×5) layer.

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The growth of copper on the Si(111)-(7×7) surface has attracted much attention scientifically as well as technologically, and Cu-on-Si is one of the most relevant metal-on-semiconductor interfaces for modern device technology. The Cu on Si interface is a strongly interacting and largely mismatched system. The intriguing structure of Cu/Si(111)-(5×5) has been investigated using a number of surface analytical techniques.[1–16] This structure can exist over a wide range of Cu coverage from submonolayer,[4] 1 monolayer (ML)[6,10,12,13,15] to 2 ML (Refs. 5, 8, 11, and 16), and a temperature range from 300 to 800 °C. Structural investigations have resulted in three different models for the local bonding, which involve three different surface stoichiometries. From angle-resolved Auger electron spectroscopy results, Chambers *et al.*[10] suggested a $CuSi_2$ structure such that the Si reconstructs from an ideal Si(111) structure to a planar geometry with Cu atoms reside at the hollow sites (H_3). Several researchers[4,6,12] favored a simple CuSi structure with Cu substituting for Si in the upper half sites (S_u) terminating the surface. Zegenhagen *et al.*[9] studied the Cu/Si(111)-(5×5) surface using x-ray standing wave and proposed a model of an almost planar, hexagonal Cu_2Si layer via Cu adsorbing in the hollow sites (H_3) and substituting for Si in the upper half sites (S_u) of the Si(111) bilayer. This model was supported by experimental data of Cu $2p$ x-ray photoelectron diffraction and high-resolution photoemission spectroscopy[13–15] and scanning tunneling microscopy.[8,16] The determination of accurate stoichiometry is essential for understanding the structure of Cu/Si(111)-(5×5).

In this work, we used scanning tunneling microscope (STM) to examine the reconstruction process and to determine precisely the Si atom density in the Cu/Si(111)-(5×5) phase. This evolution process is a key factor for understanding the nucleation and growth of the Cu/Si(111)-(5×5) structure.

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr, equipped with an Omicron variable-temperature STM and low energy electron diffraction (LEED) optics. The sample was cut to a size of 12 mm×2 mm×0.5 mm from a P-doped mirror-polished Si(111) wafer with a resistivity of 1–2 Ω cm. Atomically clean Si(111)-(7×7) surface was obtained by repetitive flashing the sample to a temperature of 1200 °C in UHV. The formation of (7×7) reconstruction was checked with STM prior to each copper deposition. The Si(111)-(7×7) surface with larger terraces of about 300 nm was chosen in our experiments in order to minimize the effect of step edges.

Copper was deposited onto the surface by resistive heating a tungsten wire wrapped with 99.99%-pure Cu wire.[17] A typical deposition rate of about 0.1 ML per minute was normally used. One monolayer of Cu is defined as the density of surface unit cells of an unreconstructed Si(111)-(1×1), i.e., 1 ML$=7.84\times10^{14}$ atoms/cm^2. The Si(111) substrate was held at about 300 °C during Cu deposition and for an additional 2 min following the deposition process. The pressure did not exceed 5×10^{-10} Torr during the deposition. For STM studies, an electrochemically etched tungsten tip cleaned by *in situ* heating was employed. All of our STM images were acquired in a constant-current mode at room temperature with a tunneling current of 0.1 nA. Due to mechanical and thermal drift, distortion exists in STM images. However, it has little effect on the evaluation of the coverage of different phases on the surface.

Si(111)-(7×7), formed spontaneously upon cleaning and annealing, is one of the most important and well-understood crystalline semiconductor surfaces. The (7×7) structure can be described with the dimer-adatom-stacking fault (DAS) model[18] as shown in Figs. 1(a) and 1(b). Each unit cell composes of two triangular subunits (faulted and unfaulted) surrounded by nine Si dimers. Furthermore, each unit cell contains 19 dangling bonds that are associated with 12 adatoms, six rest atoms and one corner hole. The bulk terminated Si(111)-(1×1) surface is essentially a bilayer: it contains two atoms in a unit mesh. Hence, the coverage of this bilayer is 2 ML. The first layer is marked as dash line; the third layer is marked as dash dot line. The height difference of two bilayers is 0.31 nm. The Si(111)-(7×7) surface has 102 Si atoms per (7×7) unit cell in layers 1, 2 and adatoms marked in Fig. 1(b), equivalent to a coverage of 2.08 ML. If the

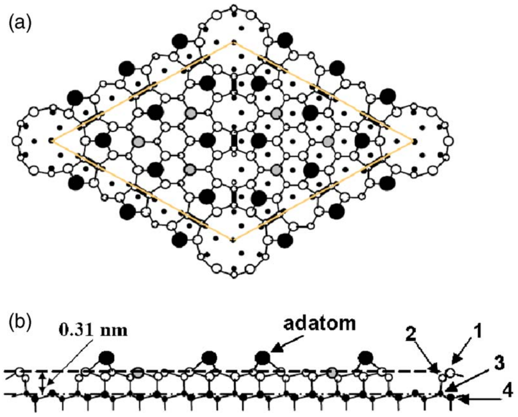

FIG. 1. (Color online) (a) Top view and (b) side view of DAS model of the Si(111)−(7×7) reconstruction. The outlined is a (7×7) unit cell with the faulted half on the left and the unfaulted half on the right. The Si atoms in the adatom layer, first, second, third, forth layer are marked in (b). First layer Si atoms are marked as dash line third layer Si atoms dash dot line.

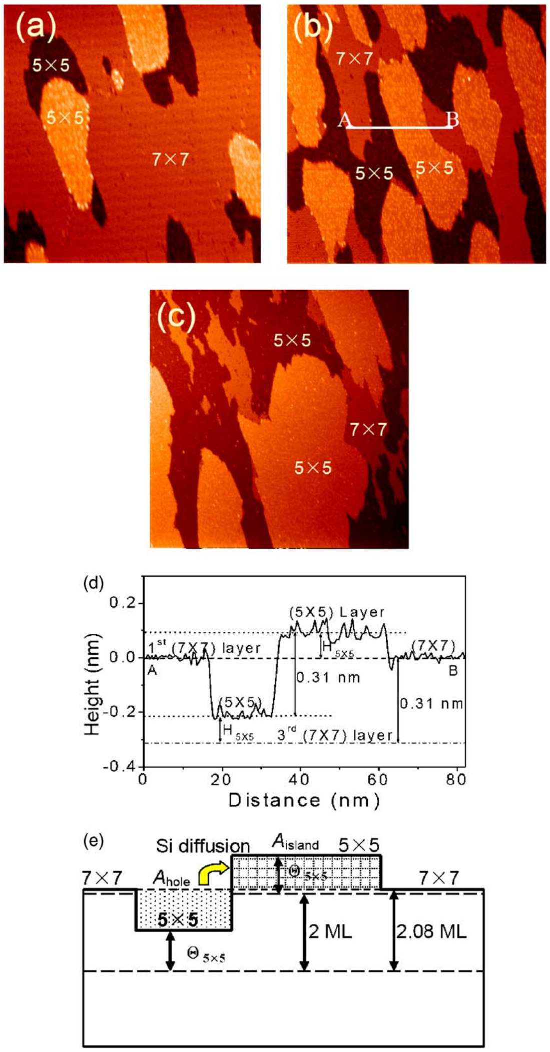

FIG. 2. (Color online) STM image (150 nm×150 nm) of "hole-island" pairs of the Cu/Si(111)−(5×5) surface phase domains formed at the Si(111)−(7×7) surface at 300 °C at different Cu coverage of 0.2 ML (a), 0.4 ML (b), and (c) 0.7 ML. The "hole" appears as dark areas and the "island" as bright areas. (d) Height profile along the line AB in (b) illustrates the height difference between the Si(111)−(7×7) and Cu/Si(111)−(5×5) surface phase. First layer Si atoms are marked as dash line; third layer Si atoms dash dot line; (5×5) layer dot line. (e) Schematic diagram illustrating the Si mass transport involved in the formation of a "hole-island" pair.

formation of the Cu/Si(111)-(5×5) phase can only consume a fraction of these Si atoms in the top layers, the excess atoms will be liberated in the (5×5) phase formation. These liberated Si atoms can combine with Cu atoms to form (5×5) islands in the layer above the original Si(111)-(7×7) surface. Quantitative analysis of the mass transport associated with the redistribution of the liberated atoms allows the determination of the Si coverage of the (5×5) phase.

Figure 2(a) shows a STM image of the early stage of the Cu/Si(111)-(5×5) phase formation after 0.2 ML Cu deposition at 300 °C. The most interesting feature is that the (5×5) phase grows in two associated domains called a "hole-island" pair. Both the bottom hole (as the dark areas in STM image) and the top island (as the bright area) display the Cu/Si(111)-(5×5) structure. The STM image of the Cu/Si(111)-(5×5) phase is similar to those reported in the literature,[5–8] but the formation of the "hole-island" pair has not been observed yet in this Cu-Si system. The formation of "hole-island" pair is a direct indication of the Si mass transport as a consequence of the difference in the top Si atom density of the Cu/Si(111)-(5×5) and Si(111)-(7×7) surfaces. The formation process involves not only the surface migration of Cu atoms but also the diffusion of Si atoms to react with them to form a 2D layer. Deposited Cu atoms migrate across the (7×7) surface and react at a suitable site to form Cu/Si(111)-(5×5) as the hole area [because it is below the adatoms of (7×7) phase]. For this reaction, only a fraction of Si atoms out of 2.08 ML in the (7×7) phase is required. Thus, the excess Si atoms are ejected onto the surrounding (7×7) region to react with Cu to form the Cu/Si(111)-(5×5) island domain. The height difference between the island and the hole should be 3.14 Å (the bilayer), which is indeed consistent with observation in the STM image.

As the copper coverage gradually increases, the areas of hole and island grow at a corresponding rate, while the area of the (7×7) reconstruction decreases. Figures 2(a)–2(c) show the STM images at different Cu coverages of 0.2, 0.4, and 0.7 ML, respectively. The (7×7) surface domain is nibbled with increasing Cu deposition. The morphological evolution of the Cu/Si(111)-(5×5) phase indicates that the surface free energy of the silicide layer must be lower than that of the clean Si(111) surface.[7] The height profile along line AB marked in Fig. 2(b) is illustrated in Fig. 2(d). The height difference ($H_{5\times5}$) between the Cu/Si(111)-(5×5) layer and the first Si(111)-(7×7) layer is about 0.1 nm, which is less than half of the height of the (7×7) bilayer structure. Therefore, the Cu/Si(111)-(5×5) structure is a compressed two-dimensional layer. The height difference of two layers of Cu/Si(111)-(5×5) phase is about 0.31 nm, which is the same as the height difference of two bilayers in

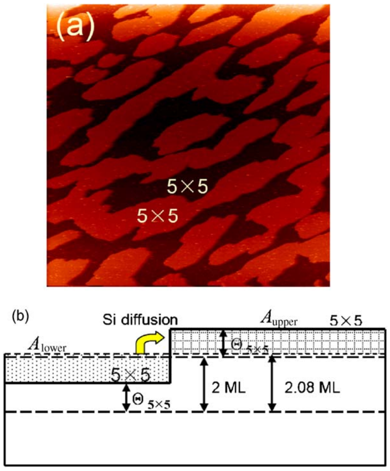

FIG. 3. (Color online) (a) STM image (250 nm × 250 nm) of the Cu/Si(111)−(5×5) surface occurring in two levels by one (111) bilayer apart after deposition 0.9 ML Cu while Si(111) substrate kept at 300 °C. (b) Illustration of the Si atoms redistribution in the formation of the Cu/Si(111)−(5×5) surface phase in two layers.

the Si(111)-(7×7) structure. The formation of Cu/Si(111)-(5×5) phase involves the Si atoms redistribution of the first bilayer, and does not affect the neighboring bilayer below it.

Noble-metal induced Si(111) surface reconstruction has been found to involve surface Si mass transport in the top Si(111) bilayer. This substantial redistribution in metal/silicon system has been reported in the formation of the Ag/Si(111)-($\sqrt{3}\times\sqrt{3}$),[19–21] Ag/Si(111)-(6×1),[21,22] and Au/Si(111)-($\sqrt{3}\times\sqrt{3}$).[23] The Si mass transport in the "hole-island" pair formation is schematically illustrated in Fig. 2(e). If taking $\Theta_{5\times5}$ and $\Theta_{7\times7}$ for the Si atom coverages in Cu/Si(111)-(5×5) and Si(111)-(7×7), and A_{hole} and A_{island} for the areas occupied by the hole and island, one can write

$$(\Theta_{7\times7}-\Theta_{5\times5})A_{\text{hole}}=(2+\Theta_{5\times5}-\Theta_{7\times7})A_{\text{island}},$$

$$\Theta_{5\times5}=\Theta_{7\times7}-2A_{\text{island}}/A,\text{where } A=A_{\text{island}}+A_{\text{hole}}$$

The resultant value of $\Theta_{5\times5}$ is 0.96±0.03 ML.

At 0.9 ML Cu deposited at 300 °C, the entire surface is covered by the Cu/Si(111)-(5×5) phase in two levels as shown in Fig. 3(a): the upper level appearing as bright and the lower level as dark area (3.14 Å lower than the former). The LEED pattern of this surface shows fractional order spots of pure (5×5) structure. The surface transformation from Si(111)-(7×7) to Cu/Si(111)-(5×5) involves the redistribution of Si atoms between the upper and lower levels. The original Si(111)-(7×7) surface contains $\Theta_{7\times7}A$ Si atoms in the top layers, where A is the total surface area. Upon formation of the Cu/Si(111)-(5×5) phase in two levels, the lower level with an area A_{lower} contains $\Theta_{5\times5}A_{\text{lower}}$ Si atoms, while the upper level accumulates $(\Theta_{5\times5}+2)A_{\text{upper}}$. The total number of Si atoms in the upper and lower domains should be the same as in the original (7×7) top layer, i.e., $\Theta_{7\times7}=2.08$ ML. The mass redistribution in the top Si layer is illustrated schematically in Fig. 3(b). The Si mass balance gives

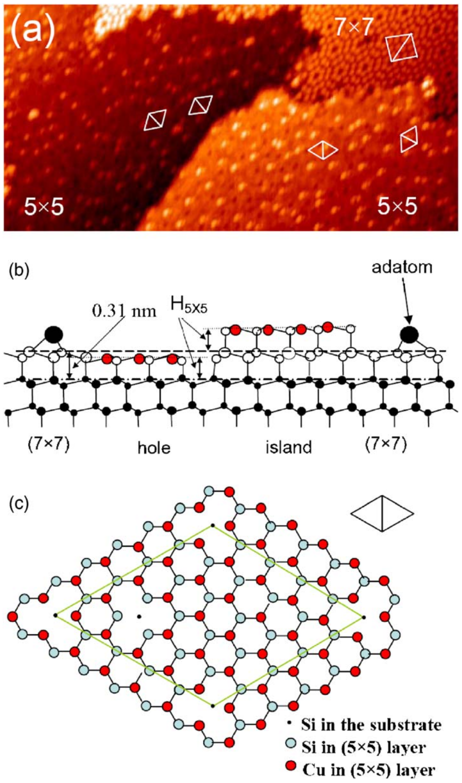

FIG. 4. (Color online) (a) High resolution STM image of coexisting Cu/Si(111)−(5×5) and Si(111)−(7×7) surface domain formed by depositing 0.4 ML Cu on Si(111) surface at temperature of 300 °C. (b) Side view of the island-hole pair of Cu/Si(111)−(5×5) and of the Si(111)−(7×7) structure. Different layers are marked as the same line symbol as that in Fig. 2(d). (c) Top view of planar model of the CuSi layer of Cu/Si(111)−(5×5) structure. One Si atom is missed on the corner and one Cu in S_u site is missed on the center.

$$(\Theta_{5\times5}+2)A_{\text{upper}}+\Theta_{5\times5}A_{\text{lower}}=\Theta_{7\times7}A,$$

$$\Theta_{5\times5}=\Theta_{7\times7}-2A_{\text{upper}}/A,\text{where } A=A_{\text{upper}}+A_{\text{lower}}.$$

The resultant value of $\Theta_{5\times5}$ is about 0.96±0.02 ML, and is consistent with the calculated value mentioned earlier. The fact that a Cu-coverage 0.9 ML is required for the complete formation of the Cu/Si(111)-(5×5) surface suggests a stoichiometric ratio of 1:1 for Cu:Si.

The high resolution STM image in Fig. 4(a) shows bright and dark dots, which clearly demonstrated that the Cu/Si(111)−(5×5) surface is not a mildly perturbed hexagonally packed Cu layer. These dark dots form a roughly triangular lattice as reported in the literature.[5,8] Our observation of equal number of Si and Cu atoms in the (5×5) surface layer is consistent with a planar CuSi structure. Based on this fact and the STM images observed in present experiment, a likely planar CuSi structure is proposed as shown in Figs. 5(b) and 5(c). Cu atoms substitute the Si atoms in the upper sites (S_u) of the Si(111) bilayer to form the Cu/Si(111)−(5×5) phase. The same surface phase is formed by Cu atoms reacting with the ejected Si atoms from the lower layer migrating onto the nearby (7×7) domain.

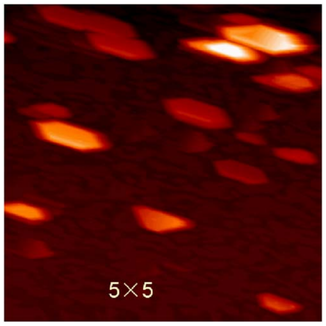

FIG. 5. (Color online) STM image (300 nm×300 nm) of Cu nanocrystals formed after deposition of 1.2 ML Cu on the Si(111)−(7×7) surface at 300 °C.

Chambers *et al.*[10] proposed a $CuSi_2$ model for the 1-ML Cu/Si(111) interface and suggested that the Si atoms in the surface bilayer reconstruct from the ideal Si(111) structure to a planar geometry with sixfold symmetry and Cu atoms residing in the hollow sites. Their results are consistent with the Cu/Si stoichiometry of Cu coverage and Si atoms in the surface bilayer. On the other hand, the Cu_2Si model was proposed by many research groups[8,9,13–16] despite the Cu coverages from submonolayer to 2 ML on Si(111) surfaces. They proposed the Cu_2Si structure in which Cu atoms adsorb at the hollow sites (H_3) and substitute the Si in the half sites (S_u) of the Si(111) bilayer. However, in these experiments they did not explain the whereabouts of the missing Si atoms in the upper bilayer sites and failed to provide reasonable explanation for the Cu_2Si stoichiometry from the deposited Cu coverage. In contrast, Chambliss *et al.*[12] reported that Cu/Si(111)−(5×5) island formation involves transport of Si from the upper to the lower terraces. The roughly equal amounts of Cu and Si is consistent with a CuSi structure. Auger electron spectroscopy[2] (AES) and thermal desorption spectroscopy[3] (TDS) measurements showed that the complete overlayer contains 0.9 to 1.3 ML Cu. Our experiments show the similar Cu coverage and the Si mass transport phenomenon in the formation process of Cu/Si(111)−(5×5) surface phase. The atomic model of (5×5) structure based on our STM observations illustrated that the Cu atoms substitute the Si atoms in the upper sites (S_u) of the silicon bilayer to form the Cu/Si(111)−(5×5) structure. The model shows two types of the crater defects that lie at the interior and the four corners of the (5×5) unit cell due to missing Cu and Si atoms respectively. We can observe the randomly distributed bright features in STM image in Fig. 4(a). The bright features reported by Mortensen[6] are randomly distributed among the (5×5) unit cells. The density of these bright features is independent of the copper coverage and annealing temperature. Kawasaki *et al.* observed the similar bright features in their STM images. They presumed the bright islands as the initial stage of crystal growth because the number of islands increases with Cu coverage. Our STM images appear to be similar to those of Kawasaki *et al.*[8] However, the density of bright dots in our STM images is independent of copper coverage and randomly distributed among the (5×5) unit cell. The strong bias dependence of the bright features may ascribe the bright features as purely electronic features with no significant geometric difference from the basic (5×5) structure.[6]

Further Cu deposition beyond the completion of the Cu/Si(111)−(5×5) surface domain results in the formation of hexagonal Cu nanocrystals. Figure 5 shows the STM image of Cu nanocrystals formed on the (5×5) interface. These Cu nanocrystals are ∼60 nm long,∼20 nm wide, and ∼4 nm high. Once the whole surface is covered by the two-level (5×5) phase, the excess Cu will form Cu nanocrystals instead of silicide layer because of the unavailability of Si atoms or the thermodynamic stability of the (5×5) CuSi layer.

In summary, the formation and evolution process of the Cu/Si(111)−(5×5) surface phase was investigated with STM. The Si mass transport takes place during the formation of (5×5) structure in two levels. From mass conservation consideration, the Si coverage in the (5×5) phase is found to be 0.96 ML. The Cu/Si(111)−(5×5) phase can accommodate 0.96 ML Si atoms and 0.9 ML Cu to form a planar CuSi silicide structure. Further Cu deposition leads to the formation of Cu nanocrystals on the (5×5) interface.

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