

Nucleation site of Cu on the H-terminated Si(111) surface

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First-principles quantum chemical calculations have been performed to clarify the nucleation site of Cu on the H-terminated Si(111) surface. The adhesion energies of a Cu atom on various sites have been obtained accurately. We have examined the following surface species as candidates for the Cu nucleation site: Si dihydride and monohydride species, fluoride, chloride, and hydroxide species, and locally oxidized sites. The basis set for Cu, which is one of the transition metals, has been chosen suitably. Results of our calculation indicate that (1) a Cu atom migrates freely on the H-terminated Si(111) surface, (2) it adheres selectively on the OH-terminated site, which is considered to exist mainly at a kink site and at the intersection of step edges, and (3) the Cu atom adhering on the OH-terminated site easily grows to a cluster.

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I. INTRODUCTION

In the manufacture of ultralarge-scale integrated circuits, it is important to investigate Cu deposition on silicon substrates not only to prevent contamination in the wet cleaning processes but also to understand the fundamental aspects of the Cu wiring technique. As the size is scaled down and the packing density increases, devices become more sensitive to trace amounts of contaminants.¹⁻⁴ Among these, the effects of Cu contamination on submicrometer devices are especially detrimental.⁵⁻⁸ The reason is that Cu spontaneously deposits on silicon substrates from HF solutions, which are inevitably used to expose the Si surface by etching Si dioxide prior to crucial process steps, such as gate oxidation, dopant diffusion, and epitaxial growth.

Recently, Cu was employed as the wiring material in a dual-damascene process⁹ to make use of its advantages of low resistivity and high resistance to electromigration. Since low resistivity of the wire materials will be even more important for future nanostructure devices, it is necessary to understand in detail the very initial stage of Cu deposition.

In the course of our attempts to form Cu nanowires¹⁰⁻¹² by means of wet processing, which is very practical in the sense that wafer scale nanofabrication is possible, we found the following facts. (1) Cu nucleation occurs immediately after immersion and (2) the positions and number density of the nuclei remain unchanged regardless of the immersion time.¹² These results were obtained in H₂SO₄ solution, and also reported in HF solution.¹³ Therefore, the identification of the initial Cu nucleation site on a bare silicon surface is the key issue in controlling Cu deposition.

Although the details of the nucleation site and the subsequent growth process have not been clarified yet, our experimental results suggested the possibility that the Si dihydride species is the nucleation site. On the H-terminated Si(111) surface immersed in H₂SO₄ solution, we found that Cu deposited exclusively on the intersection of step edges forming a convex tip, but not on those forming a concave tip.^{10,11} The convex tip consists of Si dihydride species (H₂Si=) and the

concave tip only of Si monohydride species (HSi≡). Therefore, it is deduced that Cu deposited selectively on the Si dihydride. It was also found in an experiment performed in HF solution that Cu clusters were selectively formed at kink sites of step edges, but not on the terrace.¹³ It should be noted that the kink sites of step edges are composed of Si dihydride species, and that the terraces are covered by Si monohydride species.

In this work, in order to identify the Cu nucleation site on the H-terminated Si(111) surface, we have calculated the Cu adhesion energy on the various candidates for the nucleation site by first-principles calculations based on density functional theory (DFT). We selected the candidates for the nucleation site taking the previous experimental results into account. They are Si dihydride and monohydride species, F-, Cl-, and OH-terminated species, and locally oxidized sites on the surface. Then, in order to see whether the Cu adhesion site identified can be the site for subsequent Cu growth, the Cu adhesion energy to the particular site was calculated.

II. METHOD OF CALCULATION

A. Cluster model and method

The structure of the H-terminated Si(111) surface is schematically illustrated with a ball-and-stick representation in Fig. 1. It contains an intersection of step edges denoted as *I* and a kink site denoted as *K*. The intersection is the corner of monohydride step edges in the [11 $\bar{2}$] and [$\bar{2}$ 11] directions, and it forms a convex triangular tip. Both the intersection of step edges and the kink contain Si dihydride species. In our calculation, Si dihydride and Si monohydride species were represented by the Si₃H₃ and Si₄H clusters shown by the gray spheres (Si) and solid spheres (H) in Fig. 1(b). Si dangling bonds obtained by extracting these clusters from the structure in Fig. 1(b) were terminated by H atoms to avoid artifacts due to excess spin in the quantum chemical computation. The final cluster models representing Si dihydride and Si monohydride species used for computation were Si₃H₈

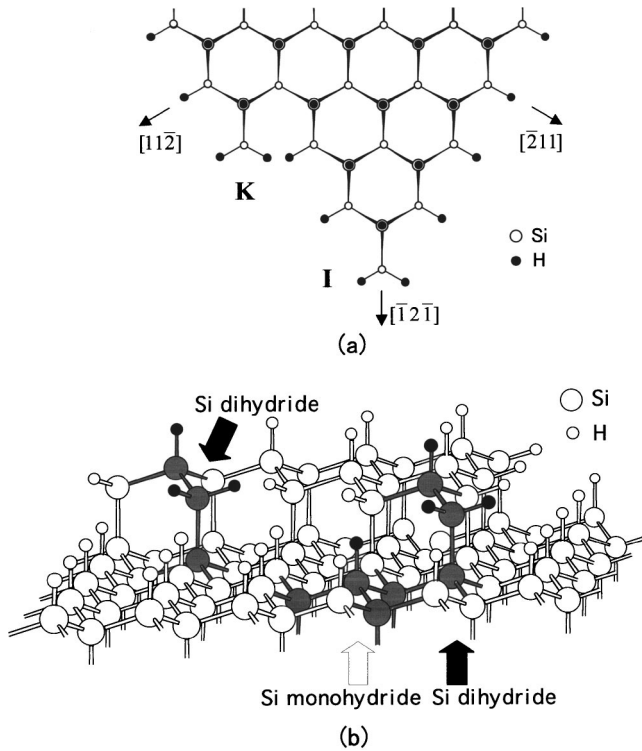


FIG. 1. Top view (a) and side view (b) of the H-terminated Si(111) surface containing an intersection (I) of monohydride step edges in the $[11\bar{2}]$ and $[\bar{2}11]$ directions and a kink site (K). (a) Filled and open circles represent H and Si atoms, respectively. Both the intersection of step edges and the kink site are composed of Si dihydride species. (b) Cluster models used in the calculation are shown with gray spheres (Si) and solid spheres (H). Filled and open arrows indicate the clusters of Si dihydride and Si monohydride species used in the computation.

and Si_4H_{10} , respectively. In this connection, it is known that the influence of the H termination is negligibly small when H atoms are located at the third nearest neighbor position or farther from the reacting atom.^{14–16}

The cluster models for the F-terminated Si site were made by replacing one of the H atoms in the Si dihydride model (Si_3H_8) and Si monohydride model (Si_4H_{10}) with a F atom. The cluster models for Cl- and OH-terminated Si sites were made in the same way. The cluster models for the locally oxidized sites on the surface were made by inserting an O atom in a Si-Si bond of both the Si dihydride model and the Si monohydride model. In this paper, we will use the term “type D structure” to refer to the Si dihydride model and the Si dihydride models modified by replacement of H with another species. Type D structures exist at a kink or an intersection of step edges. Similarly, we will use “type M structure” to refer to the Si monohydride model and the modified Si monohydride model. Type M structures are located on a terrace.

First-principles calculations were carried out using density functional theory. Throughout this work we used the B3LYP method (gradient-corrected three-parameter exchange functional due to Becke¹⁷ combined with the Lee-Yang-Parr correlation functional¹⁸). This method is known to yield accurate thermochemical properties for a wide variety

of molecular systems in comparison with the Hartree-Fock method and low-level perturbation methods.¹⁹ With respect to the adhesion energy of a Cu atom, it was reported that the B3LYP method using the cluster model^{20–22} had satisfactory accuracy as well as a coupled cluster calculation using single, double, and triplet substitutions.²² Geometry optimization was executed to determine the adhesion structures of a Cu atom on the various surface sites. During the geometry optimization, all Si, O, Cl, F, and H atoms were fully relaxed and only H atoms terminating excess Si dangling bonds were fixed at ideal crystalline positions. The adhesion energy (E_{ad}) of a Cu atom is defined as the energy released upon Cu atom adhesion to the substrate. It is computed as the energy difference between the infinitely separated state and the adhesion state. The energy of the infinitely separated state is the sum of the energies of the substrate and the isolated Cu atom.

B. Basis set

The basis functions used for Si, H, F, Cl, and O atoms were the polarized split-valence-type basis set 6-31G**. For the following two reasons, a larger basis set 6-311+G* was chosen for Cu. First, a broad d -type Gaussian function (diffuse function) should be contained in the basis set to reproduce correctly the electron configuration of the Cu atom. Basis sets without a diffuse function erroneously yield the electron configuration of the Cu atom as $[\text{Ar}]3s^23p^63d^94s^2$, which is different from the correct configuration of $[\text{Ar}]3s^23p^63d^{10}4s^1$. In such cases, the energy of the isolated state (the reference energy) is overestimated, and this causes a spurious adhesion energy. Second, among the basis sets with a diffuse function, one needs to use a basis set as large as possible to obtain the adhesion energy accurately. In fact, some small basis sets such as 3-21+G* also yield spurious adhesion energies even though they have diffuse functions. We have calculated many potential energy curves using various basis sets to judge the proper size of the basis set. The potential energy curves did not change with the size of basis sets larger than 6-311+G*. Hence, we decided to employ 6-311+G* for the Cu atom.

III. RESULTS AND DISCUSSION

A. Cu adhesion to the H-terminated sites

First of all, we compared the adhesion energy of a Cu atom to the Si dihydride species at the kink site with that to the Si monohydride species on a terrace. Figures 2(a) and 2(b) show the most stable positions of a Cu atom on the Si dihydride and the Si monohydride species, respectively. For both structures, the Cu atoms are located at a distance about 1.9 Å from the H atom along the extended line of the Si-H bond. There are no other stable sites around the Si atom. As shown in Table I, the adhesion energies of a Cu atom are 0.078 eV for the Si dihydride species and 0.088 eV for the Si monohydride species. These values are of the same order of magnitude as a typical energy of van der Waals interaction. Consequently, the adhesion of a Cu atom to the H-terminated Si(111) surface can be regarded as physisorption. In addition, there is no potential energy barrier on the path from an infi-

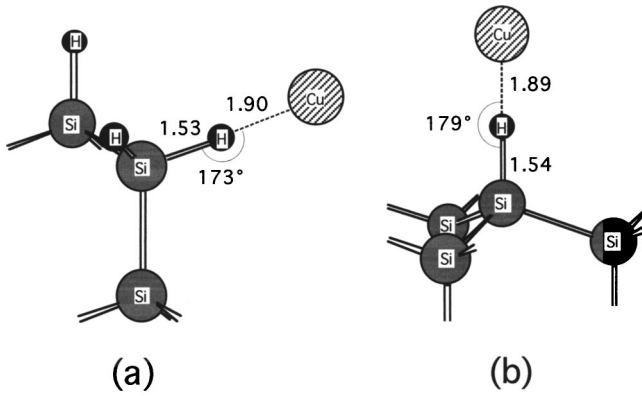


FIG. 2. The most stable atomic configurations of the adhesion state of a Cu atom on the Si dihydride (a) and the Si monohydride species (b). Bond lengths are shown in angstroms.

nite distance to the most stable position. This means that the potential barrier to the migration of Cu atoms on the H-terminated Si(111) surface is small, below 0.088 eV. In this connection, it is known that the potential barriers to Al or Ag migration on the H-terminated Si(111) surface are extremely small.^{23,24} This result indicates that Cu atoms easily migrate on the H-terminated Si(111) surface until they are trapped by particular adhesion sites as discussed later. This is consistent with our experimental results.¹²

B. Cu adhesion to the F-, Cl-, and OH-terminated sites

In this section, the Cu adhesion energy on sites where the H atom of Si dihydride and Si monohydride is substituted by other species is discussed. First, we explain why we discuss the adhesion energy of a Cu atom to the OH-terminated site. In the process of preparing atomically flat H-terminated Si(111) surfaces, selective etching of Si dihydride species in pH 8 buffered hydrofluoric acid (BHF) is used.²⁵ In the BHF solution, once the Si dihydride at the kink of the step edge is selectively removed, the neighboring Si monohydride is converted to Si dihydride. The newly formed Si dihydride is further attacked, resulting in a progressive etching along the

TABLE I. Adhesion energies of a Cu atom on Si surface sites terminated with various species.

Site		E_{ad} (eV)		Figure
H termination	Type <i>D</i>	0.078	(0.049) ^a	Fig. 2(a)
	Type <i>M</i>	0.088	(0.060)	Fig. 2(b)
F termination	Type <i>D</i>	0.114	(-0.008)	Fig. 3(a)
	Type <i>M</i>	0.109	(-0.005)	Fig. 3(b)
Cl termination	Type <i>D</i>	0.029	(0.005)	Fig. 3(c)
	Type <i>M</i>	0.021	(0.001)	Fig. 3(d)
OH termination	Type <i>D</i>	0.271	(0.164)	Fig. 3(e)
	Type <i>M</i>	0.277	(0.159)	Fig. 3(f)
Si-O-Si	Type <i>D</i>	0.101	(0.033)	Fig. 4(a)
	Type <i>M</i>	0.119	(0.055)	Fig. 4(b)

^aNumerical values in parentheses are BSSE-corrected results. (see text).

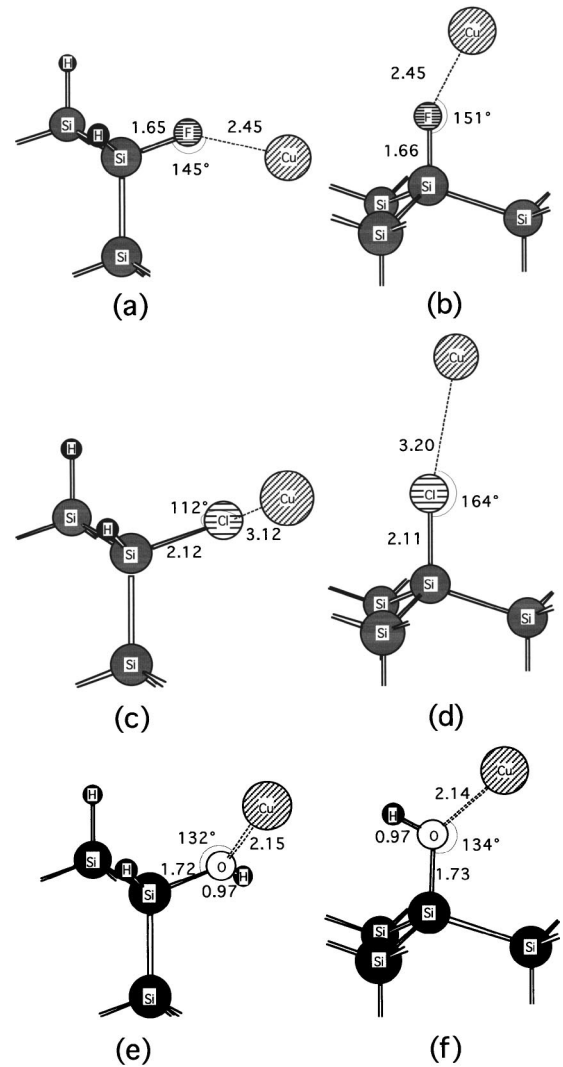


FIG. 3. The most stable atomic configurations of the adhesion state of a Cu atom on sites terminated by fluorine (a,b), chlorine (c,d), and the hydroxyl group (e,f). We considered two types of structure for each kind of terminating species; one is the structure supposed to exist at the kink site (type *D*, left column) and the other that at the terrace (type *M*, right column).

step edge. This process is called step-flow etching. It is known that the etching mechanism consists of oxidation by OH^- and subsequent anisotropic etching by H_2F^- . Hence, the H atom of the Si dihydride species can be replaced with a OH group more easily than the H atom of the Si monohydride species. The reason for choosing F- and Cl-terminated sites is as follows. F is a very common species in etchants, and Cl was found to enhance Cu deposition in solution.²⁶

Figure 3 shows the most stable atomic configurations of the adhesion state of a Cu atom on sites terminated by F, Cl, and OH. We have considered two types of structure for each kind of terminating species: one is the structure supposed to exist at the kink site [type *D*; Figs. 3(a), 3(c), and 3(e)] and the other is the structure at the terrace [type *M*; Figs. 3(b), 3(d), and 3(f)]. As in the previous calculations for the H-terminated species, the Cu atom adheres to the termi-

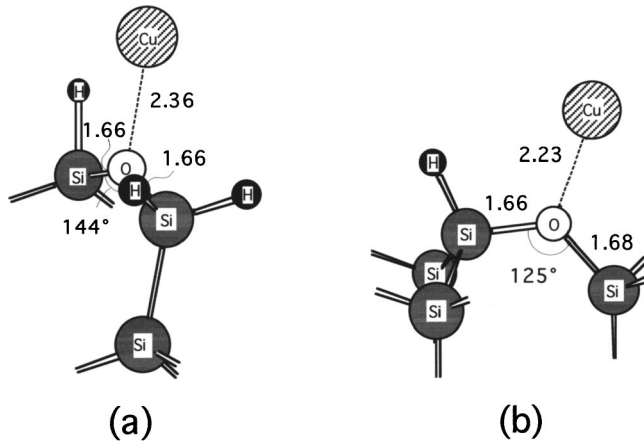


FIG. 4. The most stable atomic configurations of the adhesion state of a Cu atom on a locally oxidized site. (a) The back bond of Si dihydride is oxidized. (b) The back bond of Si monohydride is oxidized.

nating species, not to the Si atom. There are no potential energy barriers on the paths from an infinite distance to these positions.

For the fluorinated sites, the Cu atom is located at a distance of 2.45 Å from the F atom, making an angle of about 150° with the Si-F bond as shown in Figs. 3(a) and 3(b). The adhesion energy for both sites has the same value of 0.11 eV. Therefore, there is no preferred position between the kink site and the terrace site. The adhesion energy is slightly larger than that for the H-terminated species by 0.03 eV, but the difference is very small and only of the order of the thermal energy at room temperature (0.026 eV).

For the chlorinated sites, the adhesion energies and the distance from the Cl atom are 0.029 eV and 3.12 Å for the type *D* site [Fig. 3(c)], and 0.021 eV and 3.20 Å for the type *M* site [Fig. 3(d)]. These energies are very small and nearly equal to the thermal energy at room temperature. Therefore, the Cu atom is not stable on both Si fluoride and Si chloride species.

For the hydroxide sites, a Cu atom adheres to the O atom more strongly than to the other terminating species. In the adsorption state shown in Figs. 3(e) and 3(f), the Cu atom is located near the O atom. The adhesion energy and the distance from the O atom are 0.271 eV and 2.15 Å for the type *D* site [Fig. 3(e)], and 0.277 eV and 2.14 Å for the type *M* site [Fig. 3(f)]. This result means that the Cu atom binds to the O atom forming a weak chemical bond. The adhesion energies for these sites are larger than for H termination by about 0.2 eV. This energy difference is much larger than the thermal energy at room temperature. Considering that the H atom of Si dihydride is easily replaced by the OH group as mentioned above, Cu atoms migrating freely on the H-terminated Si(111) surface will adhere selectively to the OH species, which exist preferentially at kink sites and the intersections of step edges.

There is another possibility for Cu to form a chemical bond with an O atom in locally oxidized sites. We estimated the adhesion energy of a Cu atom on locally oxidized sites on the H-terminated Si(111) surface. Figure 4 shows the

most stable positions of the Cu atom adhered to the oxidized sites. Figure 4(a) shows the modified Si dihydride model in which one of the back bonds is oxidized. In Fig. 4(b), the back bond of Si monohydride is oxidized. In the adhesion state, the Cu atom is located near the O atom. This is very similar to the Cu adhesion state on silica obtained by Lopez *et al.*²⁰ It is also similar to the case of OH termination. However, the Cu-O distances are longer than those of OH termination and the adhesion energies become smaller: the energy gain is 0.101 eV for the type *D* site and 0.119 eV for the type *M* site. Consequently, the Cu atom adheres selectively only on the OH-terminated site among the possible species on the H-terminated Si(111) surface.

C. Cu adhesion to the Cu atom binding to the OH-terminated site

In order to understand the subsequent growth mechanism of a Cu cluster after the nucleation of the first Cu atom, we performed a further geometry optimization calculation to estimate the adhesion energy of the second Cu atom on the first Cu atom already adhered to the OH-terminated type *D* site. In the most stable structure, the two Cu atoms combine with each other by the orbital overlap of two 4*s* electrons. The energy gain is 2.16 eV. Consequently, the Cu atom nucleated on the OH species grows easily into a cluster.

It was reported that the etching rate of the H-terminated Si(111) surface decreased when Cu ions were contained in the BHF solution.¹³ From our calculation results, this phenomenon can be explained as follows. As mentioned above, the OH-terminated Si is a target of the etchant (H₂F⁻) during the BHF etching process. However, if Cu ions are contained in the etchant, the Cu nucleates preferentially at the OH-terminated site, and protects the target against the attack of the etchant. Thus the step-flow etching of the surface is pinned.

It is well known that triangular etch pits that are one bilayer deep and surrounded by monohydride step edges are observed on H-terminated Si(111). They are formed initially by the attack of dissolved O₂,²⁷ and subsequently by an anisotropic, step-flow etching process. Therefore, as mentioned above, there are also Si dihydride species at the sidewalls of the etch pit. Based on our calculation results, it is concluded that the triangular etch pits on the H-terminated Si(111) may also become a Cu nucleation site as well as intersections and kinks of step edges.

D. Calculation accuracy

The adhesion energies estimated in our work are very weak, so there is a concern for the effect of the basis set superposition error (BSSE). The BSSE spuriously lowers the calculated interaction energy of two clusters because individual clusters with an incomplete basis set are better described in terms of energy stabilization by utilizing the basis functions of the interaction partner.^{28–30} Numerical values in parentheses in Table I show the adhesion energies with BSSE correction by means of the counterpoise method proposed by Boys and Bernardi.²⁸ It has been pointed out by many authors^{31–33} that the counterpoise correction is, in principle, an overestimate, and the adhesion energy corrected by this method should be regarded as the minimum value of the

adhesion energy at the B3LYP level. For all termination species, the effects of the BSSE for a Cu atom are extremely small, less than 0.005 eV. This confirms that the size of the basis set employed for Cu is large enough. The BSSE has a relatively large effect on F-terminated clusters. The corrected adhesion energies become negative because of the overestimate in the counterpoise correction. The corrected adhesion energies for Cl-terminated species are almost zero. Therefore, it is deduced that the Cu atom has almost no interaction with Si fluoride and Si chloride species. After correction for the BSSE, the adhesion energies of a Cu atom for the hydroxide site are still larger than for any other species at least by 0.1 eV. Consequently, the conclusion that Cu atoms nucleate at the OH-terminated sites and grow into a cluster is unchanged after the counterpoise correction.

Since the interactions are weak, the size and shape of the cluster may influence the energy and site of Cu adhesion.³⁴ We have performed preliminary calculations using larger clusters for Si monohydride (Si_{13}H_7) and dihydride species (Si_{16}H_9). For the larger clusters, the Cu atom is located on the H atom terminating the Si surface as seen for the small cluster. With respect to the adhesion energy, the difference between the large and small clusters is very small, only of the order of 0.001 eV. Therefore, we consider that the dependence on the cluster size is sufficiently small.

It is reported that DFT generally underestimates the dispersive energy,³⁵ so our calculation may contain some error in the estimation of the dispersive interaction. However, our conclusion is consistent with many experimental facts, and it is most convincing at this stage.

IV. CONCLUSION

We performed a first-principles calculations using density functional theory to investigate the nucleation site of Cu on

the H-terminated Si(111) surface. The adhesion energies of a Cu atom on the H-, F-, Cl-, and OH-terminated sites and locally oxidized sites were calculated. The adhesion energy for OH-terminated Si is the largest (0.27 eV) of all, while those for the other sites are 0.12 eV at highest. The energy gained upon adsorption of the second Cu atom to the first Cu atom nucleated on the OH-terminated species is very large (2.16 eV). These results lead to the following two conclusions. First, the Cu atom does not adhere to the ideal H-terminated Si(111) surface, even if step edges and kink sites exist on the surface, that is, the Cu atoms migrate freely on the surface. Secondly, Cu atoms nucleate at OH-terminated sites and grow into clusters there. The Cu clusters tend to be deposited selectively at kinks and the intersections of step edges because OH-terminated species mainly exist there. These calculations are consistent with many experimental facts reported so far.

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