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Selective adsorption of metallocenes on clean and chemically modified Si(111) surfaces

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Metallocene adsorption on clean Si(111) and CaF$_2$/CaF$_1$/Si(111) substrates has been investigated with scanning tunneling microscopy. The surface chemical composition is found to strongly change the adsorption site selectivity, leading to an enhanced edge selectivity on modified substrates. Templates with well-defined local chemical reactivity have been created via self-assembly. The selective adsorption of metallocenes on such tailored substrates facilitates patterning ordered arrays of magnetic nanowires and stripes on the single digit nanometer scale. © 1999 American Institute of Physics.

INTRODUCTION

The rapid development in organometallic chemical vapor deposition, along with advanced light-induced chemical processing, has opened up the possibilities of fabricating metallic structures.\textsuperscript{1-3} Photofragmentation of the molecules removes organic ligands while leaving metal atoms behind on the surface, making it particularly attractive in developing ferromagnetic materials without incorporation of carbon or oxygen.\textsuperscript{1,3} On the micrometer scale, a variety of shapes and sizes of these structures has been achieved.\textsuperscript{1} Difficulties remain in reducing the size to the nanometer scale while preserving the uniformity of the structures, which is critical in applications. The continued trend of miniaturization provides a strong force for reducing the structure size.\textsuperscript{4} To that end, numerous studies including employing optical lithography, electron-beam writing, single atom manipulation with scanning tunneling microscope (STM), etc., have been made.\textsuperscript{1-3,5} Yet, it has been challenging to match the cost/performance requirements.

We are currently exploring the possibility for fabricating magnetic nanostructures on a large scale. In particular, we emphasize the selectivity of metallocene adsorption on stepped Si(111) surfaces as a possible route for manufacturing arrays of magnetic nanostructures. We have investigated the characteristics of the adsorption on both clean and chemically modified Si(111) surfaces. Templates with enhanced selectivity have been created by producing self-assembled stripe patterns of CaF$_2$ and CaF$_1$ on stepped Si(111) surfaces with a typical width of 5–10 nm. Whether selective deposition produces the desired growth mode for nanowires could well hinge on the chemical reactivity of such a preconditioned substrate.

EXPERIMENTAL METHOD

Si(111) wafers with 1.1° miscut towards [112] are used in the experiment. The Si(111) surface is cleaned following the procedures reported earlier;\textsuperscript{6} high-temperature flashes up to 1250 °C for approximately 10 s followed by annealing at 850 °C for 20 min and slow cool down to room temperature (about 7 min) at a base pressure $<1\times10^{-10}$ Torr. For chemical modification of the clean Si(111) surface, we choose to grow a CaF$_2$ layer because of the close match of the lattice constant between deposit and substrate as well as the insulating nature of CaF$_2$.\textsuperscript{7,8} The CaF$_2$ growth is conducted at a substrate temperature of 610 °C at a growth rate of $\sim20$ Å/min. 10 s annealing at 830 °C is followed to form a Si–Ca–F interface layer with CaF$_1$ stoichiometry, where the Ca atoms bond to Si.\textsuperscript{7} By growing 1–2 ML CaF$_2$, the CaF$_2$ stripes are formed at the upper step edges in regular arrays, covering the CaF$_1$/Si(111) interface.\textsuperscript{7,8} STM images are taken typically with a sample voltage of +4 V and tunneling current of 0.4 nA. The positive sample voltage of 4 V leads to electron tunneling from the tip directly into the conduction band of CaF$_2$.\textsuperscript{7} Thereby, disturbing effects, such as tip crash, etc. during scanning, are avoided. STM images shown in this article are in a pseudo three-dimension presentation with steps descending from left to right.

Metallocenes, one of the organic derivatives of the transition metals, have long been of interest as precursors in growing metallic microstructures via photolytic and pyrolytic processes.\textsuperscript{1,2,9} The molecule, (Cp)$_2$M, contains a metal atom (M) sandwiched between two cyclopentadienyl rings, (Cp)$_2$. The bond to the metal atom involves a π bonded system. The molecules are highly colored, stable to hydrolysis, and many melt and evaporate without decomposition. The lowest unoccupied molecular orbit-highest occupied molecular orbit (LUMO-HOMO) gap of these metallocenes is typically in the energy range from 2.5 to 5 eV.\textsuperscript{1,10} The deposition of the metallocenes is conducted in the vacuum chamber with dosing pressures varying from $5\times10^{-8}$ to $5\times10^{-6}$ Torr. STM images in Figs. 1 and 4 are taken after nickelocene exposure at room temperature. The adsorbates are nickelocene molecules. Nickelocenes are decomposed at temperatures above 100 °C.\textsuperscript{11} STM images in Figs. 3 and 6 are taken after the substrate temperature is raised above...
At room temperature the adsorbed molecules form a disordered layer on clean Si surfaces. Figure 1(a) shows an STM image of the Si(111) surface covered by nickelocene at room temperature with 900 L. The STM image of 100×100 nm² displays a single height 17 nm wide. Steps become favorable adsorption sites when Si(111) surface is covered by between 1 and 2 ML of CaF₂. Figure 1(b) shows another STM image displaying a Si(111) substrate overlaid by a single CaF₂ layer covering the CaF₁/Si interface. A substrate temperature of 610 °C and growth rate of 70 Å/min have been applied. Because of the relatively high CaF₂ vapor flux during the growth, the modified substrate shows meandering step edges, somewhat deviating from step configurations of the underlying Si(111). Figure 1(c) shows the surface after nickelocene molecules are deposited. Along the upper step edge, the adsorbed nickelocene molecules form strings with a remarkable order. In contrast, particles on terraces are randomly distributed.

Different substrates exhibit different strength of the interaction between the substrate atoms and deposits. This interaction can also be influenced by the presence of steps and other defects under certain conditions. Clean Si(111) surfaces interact strongly with metallocene molecules. Therefore, they hardly display any selectivity at room temperature. A monolayer CaF₂, on the other hand, is less reactive and exhibits weaker interactions. It allows the diffusion of molecules towards the step edge where they apparently have a higher binding energy. By chemically modifying the surface one can exercise control over the strength of the bond between the adsorbates and adsorbents. Steps and other defects, thereby, can serve as the anchors of the adsorbed molecule. In Fig. 2 we show a schematic drawing of a chemically modified substrate. With a nearly complete CaF₂ layer atop a CaF₁/Si(111) interface, step edges on this substrate become preferred adsorption sites for nickelocene molecules. In Fig. 3(a), we show an STM image of the modified substrate with a highly ordered step profile dictated by that of the Si(111) surface. We have found that the CaF₂ layer never touches the lower edge of the steps under the growth conditions described earlier. The factors controlling this effect have been discussed in previous studies. After the substrate is exposed to nickelocene vapor at room temperature followed by a brief high temperature annealing, the upper step edge is decorated by a string of adsorbates guided by the steps. Voids in the CaF₂ layer expose the underlying CaF₁/Si(111) interface. Aggregates are clustered and aligned at the edge of these imperfect sites, exhibiting a similar adsorptive behavior. These effects are illustrated in Figs. 3(b) and 3(c). Figure 3(b) is an STM image showing the substrate after room temperature deposition followed by postannealing at T = 500 °C. It displays a nearly perfect alignment of the adsorbates confined by the upper step edge. Figure 3(c) shows a similar effect owing to the defects. The lower step edge is occupied by adsorbates because the nearby CaF₁/Si(111) interface was uncovered by CaF₂. At postannealing temperatures above 100 °C, most remaining adsorbate on these sur-

**FIG. 2.** Schematic diagram of a chemically modified Si(111) showing enhanced edge selectivity for nickelocene adsorption.

**FIG. 1.** (a) Si(111) surface covered by nickelocene at room temperature with 900 L. STM image of 100×100 nm². (b) A single layer of CaF₂ atop the CaF₁/Si(111) interface with high growth rate of 70 Å/min, causing meandering steps. STM image of 150×150 nm². (c) The substrate after nickelocene exposure at room temperature with 6 L. STM image of 150×150 nm².
faces are not intact nickelocene molecules any more. They are fragments, such as nickel, acetyl cyclopene nickel, cyclopene nickel, and very little cyclopentadienyl nickel.\textsuperscript{11}

By increasing CaF\textsubscript{2} coverage, the chemical reactivity of the 2\textsuperscript{nd} CaF\textsubscript{2} layer is considerably weaker than that of the 1\textsuperscript{st} layer on top of the CaF\textsubscript{2}/Si(111) interface. Stripes of the 2\textsuperscript{nd} CaF\textsubscript{2} layer, shown as bright regions in Fig. 4, are free of nickelocene molecules even at room temperature exposure. Molecules adsorbed on the 1\textsuperscript{st} layer of CaF\textsubscript{2} exhibit the characteristic edge selectivity discussed earlier.

Selective adsorption driven by the strength of the interactions is determined by the electronic structures of the deposit and substrate. On clean Si(111), we expect a strong interaction between nickelocene and substrate. In this case, local chemical bond formation on the sites of Si dangling bonds can be expected to play a dominant role in adsorption of nickelocenes. In an earlier publication, we interpreted strong bonding between organic molecules and CaF\textsubscript{2}/Si(111) substrate in terms of energetics of the band gap of the substrate and the LUMO-HOMO gap of the adsorbate.\textsuperscript{13} Intuitively, one would expect that the chemical bonding becomes stronger as the energy overlapping of the substrate band gap and the LUMO-HOMO gap of the adsorbates increases. Meanwhile, the strong interaction between the substrate orbital and either the LUMO (if in the valence band) or HOMO (if in the conduction band) requires favorable symmetry factors.\textsuperscript{14} Accordingly, it should come as no surprise that CaF\textsubscript{2} with a broad band gap of 12 eV is not chemically reactive to nickelocene possessing a significantly narrower LUMO-HOMO gap of about 4–5 eV.\textsuperscript{1,15}

A qualitative explanation to the drastic change in the strength of the chemical reactivity of CaF\textsubscript{2} layers with different thickness can be attempted if we use a physisorption model concerning the basic van de Waals effect.\textsuperscript{16} We estimate that the strength of the electrostatic attractive interaction between the adsorbate and adsorbent is reduced at least 8 times from the 1\textsuperscript{st} to the 2\textsuperscript{nd} CaF\textsubscript{2} layer. On the 2\textsuperscript{nd} layer, this attractive interaction is considerably smaller than thermal energy of $\sim$26 meV.\textsuperscript{17} Edge selectivity on a single CaF\textsubscript{2} layer has been observed on substrates both at room temperature and elevated temperatures. It is well pronounced at elevated temperature of about 500 °C when the terrace diffusion of the adsorbates is quite rapid. Once the adsorbates arrive at the step edge, they have to overcome a diffusion barrier for descending motion across the steps. Apparently, this hindrance is caused by the adsorbates at the lower edge, which are inert and perhaps repulsive to the incoming molecules. Diffusion barriers for crossing steps have been reported previously for other systems.\textsuperscript{4,18} The molecular aggregates are also found to be clustered along the step edge, suggestive of an attractive intermolecular interaction.\textsuperscript{19} It is also indicative of the formation of an in-plane surface dipole oriented perpendicular to the step edge, leading to an attractive interaction between the adsorbates and step.\textsuperscript{19} This is
likely another important factor giving rise to the enhanced edge selectivity.

**NANOWIRE PATTERNING**

It is conceivable that the selective adsorption on a chemically modified substrate can facilitate manufacturing of metallic structures down to the single-digit nanometer scale. The option for surface modification, however, is limited by the growth modes that can be achieved. Fortunately, our choice of the combination of CaF₂/CaF₁/Si(111) assures the growth of self-assembled nanostripes, in addition to the distinctly different band gap of CaF₂ and CaF₁. The width of the CaF₂ stripes can be finely adjusted in the range of a few nm, whereas the order of the structures is self-organized during the growth. The spacing between the CaF₂ stripes can also be accurately controlled. Figure 5 is a schematic drawing illustrating the selective nickelocene adsorption on such a tailored substrate. The stripes are CaF₂ and trenches are CaF₁. The CaF₁ trenches are adsorption sites of nickelocene molecules, while the CaF₂ stripes are masks shaping the adsorbates with a desired pattern. Figure 6(a) is an STM image of an ensemble of CaF₂ stripes grown on a Si(111) surface with a CaF₁/Si interface. We expose the substrate to nickelocene vapor at temperatures. STM image of 90×50 nm². (b) Selective adsorption on CaF₂/CaF₁/Si(111) substrate by exposing the substrate to nickelocene (600 L) at substrate temperature of 500 °C. The CaF₂ stripes are free of nickelocenes at elevated substrate temperatures. STM image of 80×50 nm². (c) Similar result is obtained upon postannealing at 600 °C. Room temperature exposure of 6 L. STM image of 70×50 nm².

**SUMMARY AND OUTLOOK**

In summary, we observe changes in chemical reactivity of the substrate as we change the chemical composition of the surface. By varying the coverage of CaF₂ on Si(111), we are able to achieve selective adsorption of metallocenes with a desired pattern. Clean Si(111) displays a strong chemical reactivity, leading to a disordered layer of metallocene adsorbates at room temperature. Strong bonding on a CaF₂/Si(111) interface is also observed, presumably arising from the intermingling of the charge density of the adsorbates and substrate. In contrast, bonding to CaF₂ is very weak. Increasing CaF₂ coverage to more than 2 ML reduces the reactivity of the substrate significantly, so that the 2nd CaF₂ layer rejects metallocene molecules even at room temperature. We demonstrate a method to pattern one-dimensional metallic structures on the scale of a few nanometers on self-assembled CaF₂/CaF₁/Si(111) substrate with well-defined local chemical reactivity. As the modern technology of fabricating nanostructure has been driven to the atomic scale, such patterning is expected to play a major role in producing fine structures. A conventional patterning involves transferring a lithographically defined image in a mask on top of the substrate with a typical structure size on the micrometer scale. The patterning by means of selective adsorption has shown great potentials to overcome the limitation of traditional method in reducing the structure size. We note that most adsorbed clusters are not intact metal-
locene molecules at elevated temperatures when selective adsorption is remarkable. To ensure the growth of magnetic nanowires without carbon contamination, we need to focus on selective adsorption at room temperature. Recently, we have obtained molecular adsorption of strings of metallocenes by utilizing edge selectivity at room temperature.20 The results have shown promises in pursuing parallel fabrication of ordered arrays of magnetic nanowires.

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12 On Ag and Cu surfaces, the molecular adsorption of nickelocene has been confirmed. See Ref. 1. The molecular adsorption is also expected on Si, because Si(111) is chemically reactive.


17 An attractive electrostatic interaction arising from the basic van de Waals interaction has been estimated in the range of 40–50 meV for the 1st CaF2 layer. See Ref. 16.

