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

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(Received 16 April 1999; accepted 11 August 1999)

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.* [S0021-8979(99)01822-8]

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.[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.[1,3] On the micrometer scale, a variety of shapes and sizes of these structures has been achieved.[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.[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.[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 $[\bar{1}\bar{1}2]$ are used in the experiment. The Si(111) surface is cleaned following the procedures reported earlier:[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.[7,8] The CaF_2 growth is conducted at a substrate temperature of 610 °C at a growth rate of ~20 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.[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.[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.[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.[1,2,9] The molecule, $(Cp)_2M$, 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.[1,10] The deposition of the metallocenes is conducted in the vacuum chamber with dosing pressures varying from 5×10^{-8} to 5×10^{-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.[11] STM images in Figs. 3 and 6 are taken after the substrate temperature is raised above

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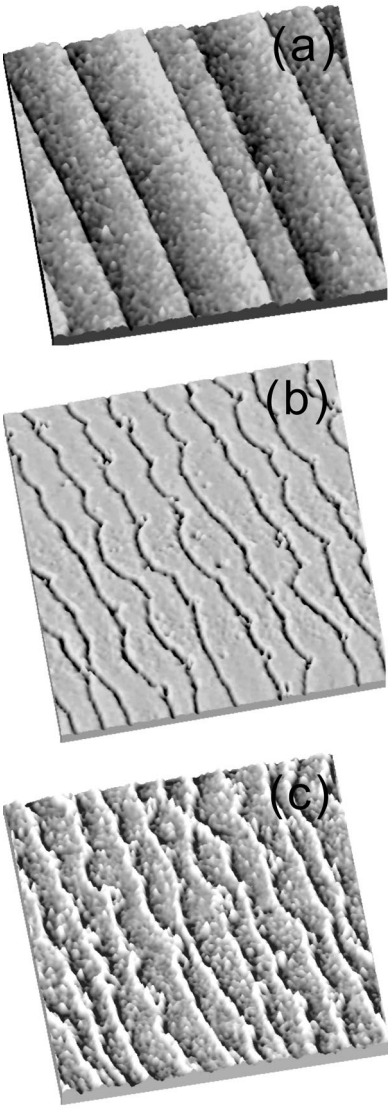

FIG. 1. (a) Si(111) surface covered by nickelocene at room temperature with 900 L. STM image of 100×100 nm^2. (b) A single layer of CaF_2 atop the CaF_1/Si(111) interface with high growth rate of 70 Å/min, causing meandering steps. STM image of 150×150 nm^2. (c) The substrate after nickelocene exposure at room temperature with 6 L. STM image of 150×150 nm^2.

100 °C due to either growth or postannealing. The adsorbates shown in these two figures are nickelocene fragments.

ADSORPTION SITE SELECTIVITY

When metallocene molecules strike a clean Si(111) surface, they bind to surface atoms predominantly in molecular form.[12] At room temperature the adsorbed molecules form a disordered layer on clean Si(111) surfaces. We have examined the surface with nickelocene exposure ranging from 6 to 900 L (Langmuir) and found no preferred molecular landing sites on this surface. Figure 1(a) is an STM image showing a Si(111) substrate covered by nickelocene molecules. The single height (0.32 nm) steps are separated by terraces of ~17 nm wide. Steps become favorable adsorption sites when Si(111) surface is covered by between 1 and 2 ML of CaF_2. Figure 1(b) shows another STM image displaying a Si(111) substrate overlaid by a single CaF_2 layer covering the CaF_1/Si interface. A substrate temperature of 610 °C and growth rate of 70 Å/min have been applied. Because of the relatively high CaF_2 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.

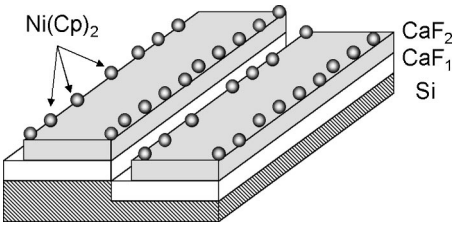

FIG. 2. Schematic diagram of a chemically modified Si(111) showing enhanced edge selectivity for nickelocene adsorption.

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 CaF_2, 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 CaF_2 layer atop a CaF_1/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 CaF_2 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.[7,8] 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 CaF_2 layer expose the underlying CaF_1/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 CaF_1/Si(111) interface was uncovered by CaF_2. At postannealing temperatures above 100 °C, most remaining adsorbate on these sur-

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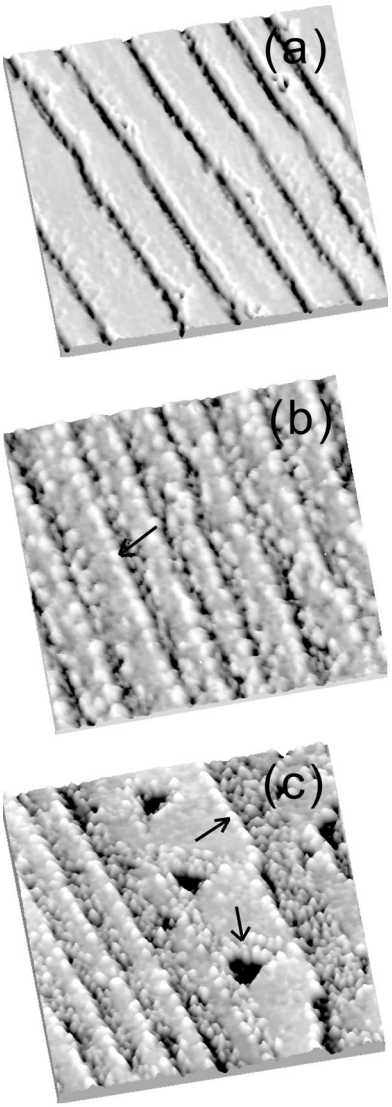

FIG. 3. (a) A nearly complete coverage of single layer CaF_2 on CaF_1/Si(111) with ordered step profile. STM image of 100×100 nm^2. (b) Strings of adsorbed nickelocene fragments are aligned along the upper edge of the steps (indicated by arrow) after room temperature adsorption followed by postannealing at 500 °C. 900 L. STM image of 100×100 nm^2. (c) Preferred adsorption sites along the edges of voids (indicated by arrows). Room temperature exposure of 600 L. STM image of 100×100 nm^2. Adsorbates on the lower edge of the steps are bound to surface atoms on a CaF_1/Si(111) interface.

faces are not intact nickelocene molecules any more. They are fragments, such as nickel, acetyl cyclopropene nickel, cyclopropene nickel, and very little cyclopentadienyl nickel.[11]

By increasing CaF_2 coverage, the chemical reactivity of the 2nd CaF_2 layer is considerably weaker than that of the 1st layer on top of the CaF_1/Si(111) interface. Stripes of the 2nd CaF_2 layer, shown as bright regions in Fig. 4, are free of nickelocene molecules even at room temperature exposure. Molecules adsorbed on the 1st layer of CaF_2 (darker areas in Fig. 4) exhibit the characteristic edge selectivity discussed earlier.

Selective adsorption driven by the strength of the interactions is determined by the electronic structures of the de-

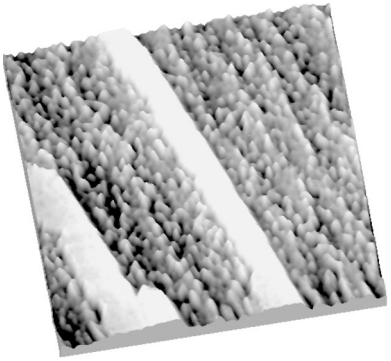

FIG. 4. The 2nd CaF_2 layer is not chemically reactive after room temperature exposure. The bright stripes show areas covered by the 2nd CaF_2 layer, and are free of molecules at room temperature. 900 L. STM image of 150 ×150 nm^2.

posit 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_1/Si(111) substrate in terms of energetics of the band gap of the substrate and the LUMO-HOMO gap of the adsorbate.[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 valance band) or HOMO (if in the conduction band) requires favorable symmetry factors.[14] Accordingly, it should come as no surprise that CaF_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.[1,15]

A qualitative explanation to the drastic change in the strength of the chemical reactivity of CaF_2 layers with different thickness can be attempted if we use a physisorption model concerning the basic van de Waals effect.[16] We estimate that the strength of the electrostatic attractive interaction between the adsorbate and adsorbent is reduced at least 8 times from the 1st to the 2nd CaF_2 layer. On the 2nd layer, this attractive interaction is considerably smaller than thermal energy of ~26 meV.[17] Edge selectivity on a single CaF_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.[4,18] The molecular aggregates are also found to be clustered along the step edge, suggestive of an attractive intermolecular interaction.[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.[19] This is

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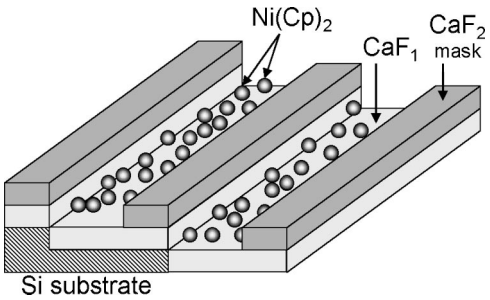

FIG. 5. Schematic diagram of $CaF_2/CaF_1/Si(111)$ substrate for selective nickelocene adsorption.

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 $CaF_2/CaF_1/Si(111)$ assures the growth of self-assembled nanostripes, in addition to the distinctly different band gap of CaF_2 and CaF_1, ~12 eV vs 2.4 eV. The accumulated knowledge now puts us in a position to devise a template containing precisely arranged stripes with alternating local chemical reactivity with a periodicity of 10–20 nm.[7] We expect the metallocene molecules to be rejected in regions covered by CaF_2 while being accepted in places with CaF_1. The width of the CaF_2 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 CaF_2 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 CaF_2 and trenches are CaF_1. The CaF_1 trenches are adsorption sites of nickelocene molecules, while the CaF_2 stripes are masks shaping the adsorbates with a desired pattern. Figure 6(a) is an STM image of an ensemble of CaF_2 stripes grown on a Si(111) surface with a CaF_1/Si interface. We expose the substrate to nickelocene vapor at temperature of 500 °C, and the adsorbates are selectively deposited in the CaF_1 trenches. Because bonding to CaF_2 is very weak, no adsorption takes place at the elevated growth temperature [see Fig. 6(b)]. In another experiment, we manage to utilize CaF_2 stripes as masks upon postannealing at $T=600\,°C$ while depositing molecules at room temperature. As shown in Fig. 6(c), the CaF_2 stripes are free of adsorbates, resulting from thermal desorption of nickelocenes. We note that at elevated substrate temperature, most adsorbates are nickelocene fragments.[11] We have also found similar adsorptive behavior of several other metallocenes, such as ferrocene, etc.

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 CaF_2 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 $CaF_1/Si(111)$ interface is also observed, presumably arising from the intermingling of the charge density of the adsorbates and substrate. In contrast, bonding to CaF_2 is very weak. Increasing CaF_2 coverage to more than 2 ML reduces the reactivity of the substrate significantly, so that the 2nd CaF_2 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 CaF_2/CaF_1 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-

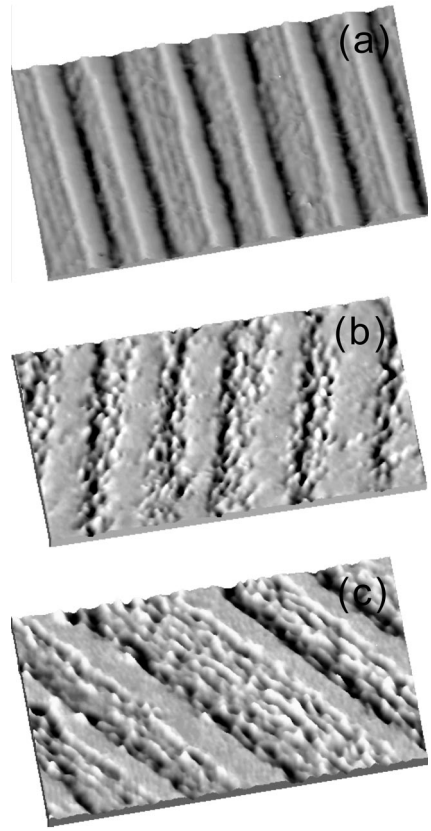

FIG. 6. (a) $CaF_2/CaF_1/Si(111)$ substrate before deposition. The width of CaF_2 stripes is ~5.6 nm, and CaF_1 trenches is ~12 nm. STM image of 90×50 nm^2. (b) Selective adsorption on $CaF_2/CaF_1/Si(111)$substrate by exposing the substrate to nickelocene (600 L) at substrate temperature of 500 °C. The CaF_2 stripes are free of nickelocenes at elevated substrate temperatures. STM image of 80×50 nm^2. (c) Similar result is obtained upon postannealing at 600 °C. Room temperature exposure of 6 L. STM image of 70×50 nm^2.

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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.

ACKNOWLEDGMENTS

We thank D. Y. Petrovykh, Dr. J. Viernow, and Dr. T. A. Jung for many useful discussions. This work is supported by NSF under Award Nos. DMR-9624753, DMR-9632527, and DMR-9815416.

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