Formation of Well-Ordered Step Structures on Si(111) by a Combination of Chemical Etching and Surface Scratching for Producing Macrosized Patterns

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Scratching of H-terminated Si(111) surfaces with Teflon tweezers, followed by etching with 40% NH_4F, led to formation of well-ordered patterns of surface crystal steps, in contrast to the case of no scratching. The scratching produced surface damage in the form of nanowires, and the step patterns changed in shape by altering the direction of scratching. The results were explained on the basis of a reported mechanism for NH_4F etching at the Si(111) surface by assuming that step etching stopped at the scratch-induced nanowires of damage. It is suggested that a combination of controlled macrosized patterning and chemical etching provides a new promising approach to well-regulated nanostructuring at the Si surface.

Introduction

Nanostructuring at semiconductor surfaces, which constitutes the basis of future devices such as quantum-confined optical and electronic devices, has been attracting keen attention in the field of semiconductor sciences and technologies. Much effort has been made to find and develop new structuring techniques that have the fabrication size significantly smaller than the limit of conventional photolithography. Of several approaches proposed, a chemical approach to make use of the self-assembling or self-organizing ability of molecular systems has attracted growing attention because it has a strong merit in that it can be adapted to mass production, which is inevitably necessary for practical application. It can be noted that another important approach of atomic-scale fabrication by use of surface-probe microscopes such as scanning tunneling microscopy and scanning near-field optical microscopy lacks this merit.

In the chemical approach, the control of arrangement of surface crystal steps is of great importance because the steps can act as active sites for further surface modification with functional molecules or metals.[1,2]

Recently, some studies have been made along this line. Ogino et al.[3] reported the formation of regular arrays of step bunches by applying high-temperature annealing to Si(111) surfaces having hole arrays fabricated by photolithography-based ion etching. Finnie et al. later used the step bunches as a template for selective epitaxial growth.[4] On the other hand, Omi et al. reported the formation of well-ordered arrangements of atomic steps by deposition of Si on a Si(111) surface with a mesa pattern by a molecular beam epitaxial method.[5]

In the present paper, we report a much simpler method to form well-ordered step patterns at the Si(111) surface. We have found that a combination of chemical etching with surface scratching that produces a damage pattern acting as a macrosized template of nonreactive nature forms amazingly well-ordered nanopatterns of surface crystal steps.

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Experimental Section

Single-crystal *n*-type silicon (*n*-Si) wafers of a resistivity of ∼1−5 Ω cm, having the (111) face with a miscut angle of $0.36 \pm 0.1°$ in the $\langle\bar{1}\bar{1}2\rangle$ direction, were obtained from Osaka Tokushu Gokin Co., Ltd., Japan. They were cleaned by the ordinary RCA cleaning method[6] and successively etched with 5% HF for 5 min and 40% NH_4F for 15 min to obtain H-terminated surfaces with a step-terrace structure.[7] A macrosized pattern, acting as a template for formation of a well-ordered step pattern, was introduced in the present work by simple scratching of the Si(111) surface with Teflon tweezers in a 40% NH_4F solution at a stage just after the Si surface was immersed in it for etching.

Results and Discussion

Figure 1 shows (A) an atomic force microscopic (AFM) image of the *n*-Si(111) surface obtained by the above-mentioned treatment (surface scratching and NH_4F etching) compared with (B) an AFM image of the *n*-Si(111) surface treated with no scratching. Quite well-ordered patterns of surface crystal steps with uniform spacing are produced in Figure 1A between scratch-induced (white) wires running nearly in parallel with each other in the $\langle\bar{1}\bar{1}2\rangle$ direction. This is in sharp contrast to the step pattern in Figure 1B, which is normally obtained by NH_4F etching of a Si(111) surface with a small miscut angle in the $\langle\bar{1}\bar{1}2\rangle$ direction. The steps in Figure 1A are composed of monohydride Si atoms, namely, they are monohydride (Si−H) steps or $\langle 11\bar{2}\rangle$ steps, as discussed later. The chemical composition and structure of the scratch-induced wires are unclear at present, but our experiments have shown that they only play a role as a stopper of surface step etching, as also discussed later. Thus, the above result clearly indicates that a combination of macrosized nonreactive patterns (such as scratch-induced nanowires) and chemical etching leads to formation of well-ordered patterns of surface crystal steps. Many more ordered step patterns can be formed if a more regulated macrosized pattern is produced by, for example, photolithography.

The distance between the adjacent Si−H steps in the ordered step patterns in Figure 1A can be controlled easily by altering

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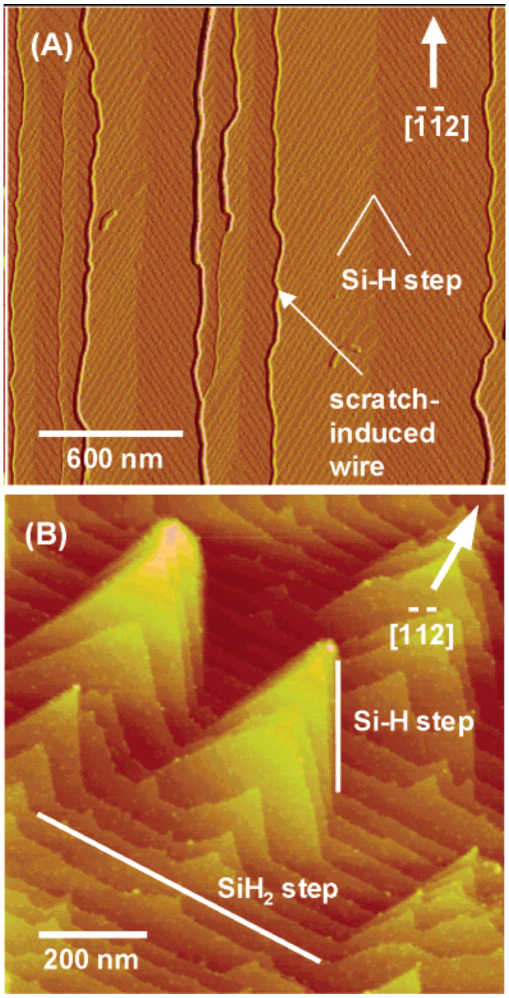

Figure 1. (A) An AFM image of an H-terminated Si(111) surface after it was scratched and etched with 40% NH_4F for 15 min. (B) An AFM image of the Si(111) surface treated in the same way as in (A) except that no surface scratching was given. See text for details.

the miscut angle of the Si(111) wafer. Another notable point is that various step patterns can be obtained by changing the direction of scratching with respect to the $\langle \bar{1}\bar{1}2 \rangle$ direction of the Si(111) surface. In general, the scratch-induced wires lie nearly in parallel with the direction of scratching. When the scratch-induced wires are in the $\langle \bar{1}\bar{1}2 \rangle$ direction, as is the case in Figure 1A, quite symmetric step patterns are produced between two adjacent scratch-induced wires (Figure 1A). On the other hand, when the scratch-induced wires are in a direction inclined from the $\langle \bar{1}\bar{1}2 \rangle$ direction by about 30° or more, the ordered step patterns are produced only on one side of the scratch-induced wires. Figure 2 shows an example of such surface step patterns; the scratch-induced wire is inclined left from the $\langle \bar{1}\bar{1}2 \rangle$ direction by about 30°, and the ordered step pattern is produced only on the left-hand side of the scratch-induced wire. Inversely, in the case where the scratch-induced wires are inclined right, the ordered step patterns are produced only on the right-hand side of the wires. It is to be noted that in Figure 2, a large gap stair is formed on the opposite side of the ordered step pattern, adjacent to the scratch-induced wire. All these results indicate that a combination of macrosized patterns with chemical etching can produce a variety of ordered step patterns.

How are such well-ordered step patterns produced? Figure 3 shows a time course of the surface step structure during the NH_4F etching in a range of the etching time from 2 to 15 min

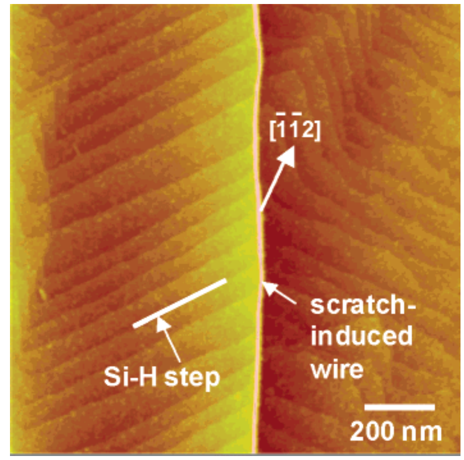

Figure 2. An AFM image of the surface step pattern of another type, obtained in the case where the scratch-induced wire is in a direction inclined from the $\langle \bar{1}\bar{1}2 \rangle$ direction.

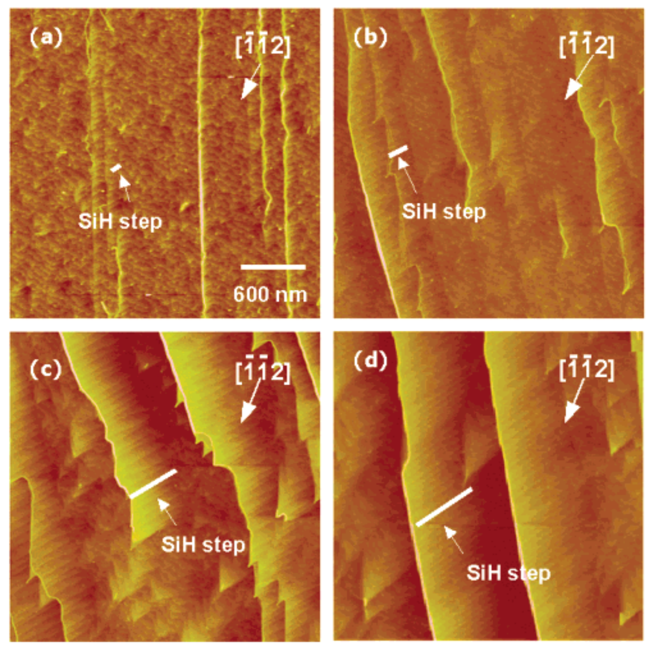

Figure 3. A time course of the surface step structure during the NH_4F etching after the surface scratching. The etching time: (a) 2 min; (b) 5 min; (c) 10 min; and (d) 15 min.

after the surface scratching. The scratch-induced wires in this case are in a direction inclined left from the $\langle \bar{1}\bar{1}2 \rangle$ direction by about 30°. The well-ordered step patterns start to be produced from the positions of scratch-induced wires (Figure 3a), and they extend longer and longer with the etching time in the direction opposite to the scratch-induced wires (parts b and d of Figure 3).

The above result can be explained reasonably on the basis of a reported mechanism of the NH_4F etching of the Si(111) surface.[8−11] Let us first consider a nonscratched Si(111) surface with a small miscut angle in the $\langle \bar{1}\bar{1}2 \rangle$ direction. The NH_4F etching in general leads to formation of linearly extending dihydride (SiH_2) steps (or $\langle \bar{1}\bar{1}2 \rangle$ steps) perpendicular to the $\langle \bar{1}\bar{1}2 \rangle$ direction, though they are interrupted here and there by triangular “hillocks” with monohydride (Si−H) steps (or $\langle 11\bar{2} \rangle$ steps), as seen in Figures 1B and 4A. The formation of the triangular “hillocks” is simply because the dihydride SiH_2 steps are chemically reactive and easily etched, compared with the monohydride Si−H steps, and it is explained by Hines et al. in the following:[9] The NH_4F etching first produces atomic kinks

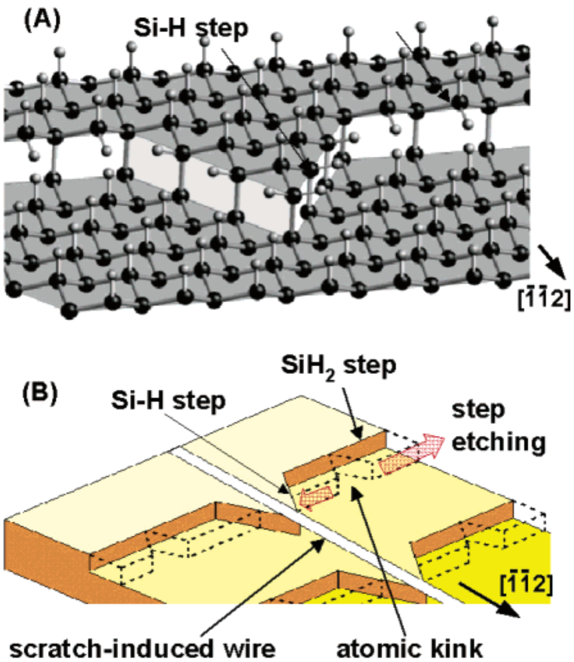

Figure 4. (A) Schematic atomic model of dihydride (SiH_2 or $\langle\bar{1}\bar{1}2\rangle$) and monohydride (Si−H or $\langle 11\bar{2}\rangle$) steps for the Si(111) surface with a small miscut angle in the $\langle\bar{1}\bar{1}2\rangle$ direction. (B) Schematic illustration of step etching at the SiH_2 steps, leading to formation of an ordered step pattern.

at the SiH_2 steps (by removal of Si atoms), and then step etching proceeds from the reactive kink sites along the SiH_2 steps (Figure 4B). The step etching is finally stopped when the reacting kink site has reached a stable monohydride (Si−H) step. Successive occurrence of such kink-site formation, step etching, and its stopping easily leads to the production of the triangular hillocks composed of the monohydride steps.

The production of the well-ordered step patterns such as those shown in Figure 1A can be explained by a similar mechanism if we assume that the step etching at the dihydride steps is stopped when it has reached the scratch-induced wires (Figure 4B). This assumption is not unreasonable because the scratch-induced wires are expected to be a kind of surface damage of nonreactive nature. The production of different step patterns depending on the scratching direction (Figure 2) can also be explained by the above mechanism. When the scratch-induced wires are in the $\langle\bar{1}\bar{1}2\rangle$ direction, the angle between the wires and the Si−H steps is 30° on both sides of the wires and thus the well-ordered Si−H steps are produced symmetrically with respect to the wires, as is really seen in Figure 1A. On the other hand, when the scratch-induced wires are in a direction inclined from the $\langle\bar{1}\bar{1}2\rangle$ direction by more than 30°, the angle between the wires and the Si−H steps has a meaningful (positive) value only on one side of the wires, as can be understood from Figure 4B, and thus the well-ordered Si−H steps can be produced only on one side of the wires.

Conclusion

The present work has revealed that a combination of macrosized patterning by surface scratching and NH_4F etching for H-terminated Si(111) surfaces leads to the formation of well-ordered patterns of monohydride (Si−H) steps. The result can be explained if we assume that step etching is stopped at scratch-induced wires of damage at the Si(111) surface. Production of more regulated macrosized patterns of nonreactive nature by, e.g., photolithography would lead to formation of more ordered step patterns. The present work thus provides a new promising approach to nanostructuring since surface steps can be used as active sites for further surface modification.

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