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STM Observations of Surface Nanostructures on Si (111) Formed after Synchrotron Radiation Stimulated Cleaning

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Nanostructures on Si (111) surfaces formed after synchrotron radiation stimulated cleaning (oxide removal) were observed for 0°±0.1° and 4°±0.5° misoriented toward $[11\bar{2}]$ samples by scanning tunneling microscopy. The surface of 0° off showed large regions of atomically flat Si (111)- 7x7 structure, and was characterized by the formation of single bilayer steps nicely registered to the underlying crystal structure, clearly different from the disordered step edge obtained by the usual high temperature thermal cleaning. The 4° misoriented sample showed nearly uniformly spaced step bunches and terraces terminated by 7x7 unit cells in both SR stimulated and thermal cleanings.

keywords: nanostructure, synchrotron radiation, scanning tunneling microscopy, Si (111), SiO_2 desorption, step alignment

1. INTRODUCTION

Semiconductor processes using synchrotron radiation (SR) photochemical reaction [1-3], have many advantages such as lower damage in comparison with plasma processes, high spatial resolution and aspect ratio because of the shorter wavelengths, and the applicability to thick insulating materials where charged particles in electron beam lithography cannot be used. Some of these advantages have been demonstrated in SR stimulated cleaning on Si surfaces [2,4-6]. In a pure thermal cleaning, the Si wafer has to be heated to > 850°C and, additional long hours (usually 20 h) of annealing at 700 °C is required to obtain the thermal equilibrium surface [7,8]. In an SR stimulated process, the desorption occurs at much lower temperatures (650-700°C) and atomically flat surfaces free of voids, which inevitably appear in a pure thermal desorption at these low temperatures [9], can be obtained [4-6].

In this paper, we report investigations using scanning tunneling microscopy (STM) on the surface morphology of singular and vicinal Si (111) after cleaning by SR irradiation. The singular surface showed large regions of an atomically flat and coherent 7x7 structure. An interesting feature of the surface was the formation of single bilayer steps nicely registered to the underlying crystal structure and the width quantized (to the unites of 7x7 unit cell) of stripes formed by the bilayer steps. The vicinal surfaces were used for an ordered step structure by the terrace width quantization.

2. EXPERIMENTS

The SR stimulated cleaning and STM observation were performed at the UVSOR beamline 4B in the Institute for Molecular Science. The energy distribution of the SR beam ranged from about 1000 to a few electron volts with the maximum at around 100 eV. The calculated photon flux was 1.2 x 10^{16} photons/cm^2 for an average ring current of 100 mA. The beam spot on the sample surface was an ellipse with a major diameter of 5mm and a minor diameter of 3 mm. The STM measurements were performed with a Rasterscope-3000 from DME Co. The base pressure of the STM chamber was 5 x 10^{-10} Torr. Details of the experimental conditions are described in Ref. 4. The sample (3 x 8 mm^2) was a boron doped p-type Si wafer with thickness of 0.5 mm and resistivity of 8 Ωcm. The surfaces used were singular and vicinal (111). On the singular surface the misorientation was less than ±0.1°, while on the vicinal surface the misorientation was 4° ± 0.5° toward $[11\bar{2}]$.

A native oxide layer was formed on the Si substrate by a conventional wet process [4]. The thickness of the native oxide layer was about 1 nm [10]. The sample was resistively heated by passing a current through it and the temperature maintained within ±10 °C as monitored with an optical pyrometer. The sample temperature was decreased after cleaning by the rate of 1°C/s down to 700°C and below this by 2°C/s.

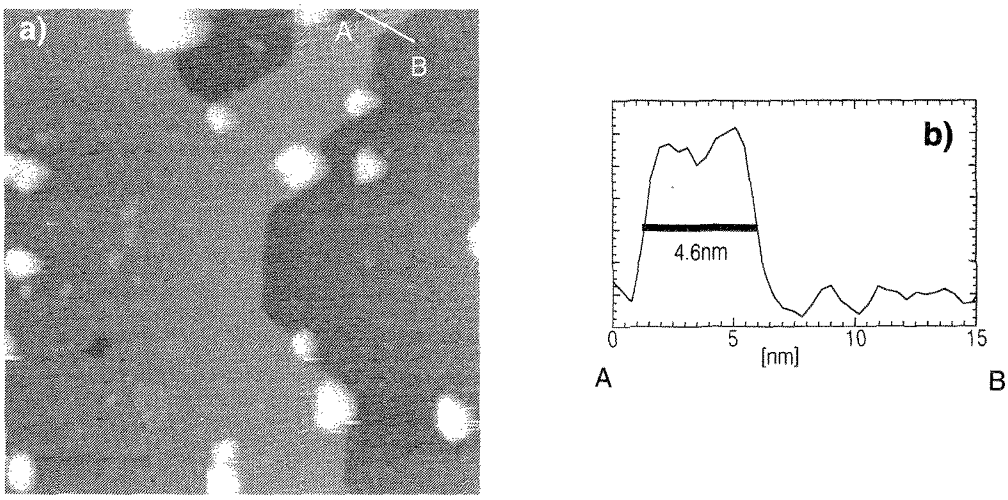

Figure 1. (a) 100 nm x 100 nm STM topograph of a Si (111) singular surface after 5 h of SR irradiation at 650°C. (b) Line profile across the stripe at the upper-right-hand side coner of (a).

3. RESULTS AND DISCUSSION

Figure 1(a) shows an STM topography of a Si (111) singular surface after 5h of SR irradiation at 650°C. The Pt/Ir tip was biased at -2.1 V with respect to the sample. The tunneling current was kept at 0.14 nA. The other STM images shown in this article have similar parameters. Steps and terraces were observed on the surface clearly, indicating that the oxide film made by the wet chemical process were desorbed completely. The desorption rate of SiO_2 was estimated to be 10^{-7}/photon.

The most striking feature of the topography is the single bilayer steps aligned to low index of the surface lattice even by the low temperature treatment. Such an alignment gives the steps an hexagonal appearance in places. Some irregularly shaped dust particles are also visible, and possibly due to residual SiO_2 or carbon contamination. These particles act as pinning centers of the steps that define the overall shape of the steps. The registry of the steps to the underlying crystal creates interesting structures. For example, at the upper right corner in Fig 1(a), a terrace stripe 4.6 nm wide has formed along $[0\bar{1}0]$ as seen in the line profile of Fig. 1(b), which is the width of only one 7x7 unit cell. It suggests that steps are aligned along the boundaries of the 7x7 unit cell.

The effect on the step alignment was confirmed by a higher resolution STM image. Figure 2 (a) shows the atomic image of the sample shown in Fig. 1(a). The 7x7 structure is clearly visible. The displacement vector g(a, b) between upper and lower terrace 7x7 structures defined by Goldberg et al. is measured to be g(1+1/3, 3+2/3) at this step [8]. This indicates that the step is F6a (according to the definition given by Tochihara et al. [11]) descending along $[11\bar{2}]$. The 7x7 structure is coherent over all of the surface observed by STM (max $100 \times 100\ nm^2$), and the width of the bilayer stripes are all quantized to units of the 7x7 cell width similar to that observed in the terrace width of a thermal equilibrium Si(111) surface [7]. These facts indicate that the SR irradiated surface is in thermal equilibrium.

Interesting is the comparison of this result with the usual high temperature thermal decomposition of the thin SiO_2 film, which is so called a thermal cleaning process. In Fig. 2(b), the step edge structure of the Si (111) surface prepared by thermal desorption at 880°C for 1 min was observed by STM. It is clear that the step edge is disordered and far from the thermal equilibrium. It is reported that long time (700°C 20h) annealing is required to get a thermal equilibrium Si (111) vicinal surface [7] after the usual high temperature cleaning. Therefore, SR stimulated cleaning is very unique in the meaning that thermal equilibrium surface is obtained easily at low temperatures at which even SiO_2 film de-

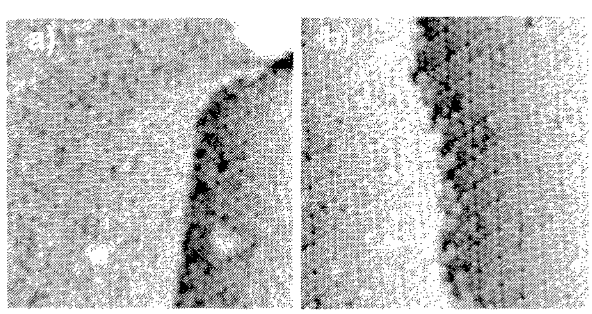

Figure 2. (a) 25 nm x 25 nm STM image of the sample shown in Fig. 1 (a). It is observed that the bilayer step aligns along boundaries of the 7x7 unit cell. (b) 25 nm x 25 nm STM image of the sample prepared by the thermal cleaning of 880°C 1min. It is clear that the step edge is disordered and far from the thermal equilibrium.

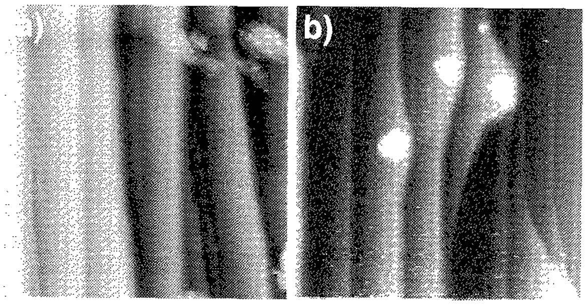

Figure 3 200 nm x 200 nm STM images of the Si (111) 4° misoriented toward $[11\bar{2}]$ surface after the 880°C 1min thermal (a), and the 700°C 2h SR stimulated cleaning (b), respectively.

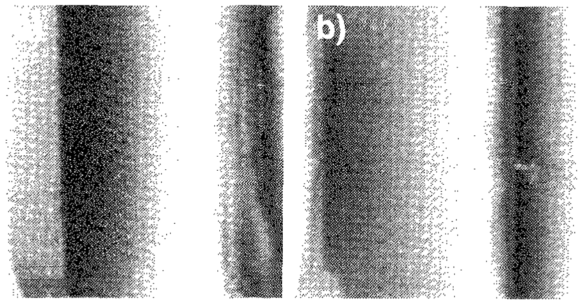

Figure 4 (a) and (b) are expanded STM images (50 nm x 50 nm) of the samples shown in Figs. 3(a) and (b), respectively.

composition cannot be observed.

We used this SR stimulated cleaning to the vicinal surfaces in order to obtain an ordered structure of the straight steps separated by constant-width terraces. The vicinal surface of which normal was tilted by 4° from (111) toward $[11\bar{2}]$ was used for this purpose. The steps are expected to lie every 4.5 nm nearly corresponding to the one unit cell width of 7x7 structure. On the vicinal surface, it is known that the step bunching occurs and terraces become wider than that estimated from the misorientation angle after thermal processes [12-14].

The tilt direction and angle of the surface affect the step structure. In the case of vicinal surface misoriented toward $[11\bar{2}]$, the STM images after slow cooling shows nearly uniformly spaced and sized step bunches consisting of ~10 steps each for 2.5° misorientation [12], and this step bunching forms the (331) facet for 10° misorientation [13]. These results were obtained by using thermal cleaning at high temperatures (~1200°C) where the Si surface has 1x1 structure. The surface phase transition from 1x1 to 7x7 reconstruction during cooling process makes the step alignment change drastically, involving the step bunching and the terrace width expansion. The SR stimulated cleaning, on the other hand, has no such a high temperature process with the surface phase transition. Therefore, it is expected that the step structure changes gently. This difference of the surface structure rearrangement after the oxide removal may be one of the reasons for the clear difference of the step structures on the singular surfaces shown in Figs. 2 (a) and (b).

Figures 3 (a) and (b) show STM images of the vicinal Si (111) surface misoriented 4° toward $[11\bar{2}]$ after the thermal and the SR stimulated cleanings, respectively. The sample shown in Fig. 3(a) was prepared by thermal desorption of oxide at 880 °C for 1 min. The sample shown in Fig. 3 (b) was prepared by SR stimulated cleaning (700°C 2h SR irradiation).

In both STM images, nearly straight step bunches consisting of ~8 steps are observed similarly to the STM image observed in the 2.5° misorientation [13]. High resolution images corresponding to Figs 3(a) and (b) are shown in Figs 4 (a) and (b), respectively. These figures show terraces with the 7x7 structure and step bunches more clearly. The surface formed by step bunching shows ~22° inclined facet (roughly the same as the (331) facet). Almost all the terrace edges were observed to align along the boundaries of the 7x7 unit cells. These results indicate that both of thermal and SR stimulated cleaning give almost thermal equilibrium surfaces in the case of 4° misorientation, different from the singular surface case.

In the case of 4° misorientation surfaces, the density of the migrating adatoms which are generated at the step edge, are significantly high. This large number of migrating adatoms is considered to be sufficient to make the surface flat and the steps straight for both 700°C 2h SR stimulated and 880°C 1min thermal cleanings.

4. CONCLUSIONS

The SR process on Si (111) surface were used for formation of nanostructures. The 0° (±0.1°) and 4° (±0.5°) misoriented Si (111) surfaces were observed by STM after desorption of surface SiO_2 by SR stimulated cleaning. The 0° off surface showed large regions of atomically flat Si (111)- 7x7 structure, and was characterized by the formation of single bilayer steps nicely registered to the underlying crystal structure. It indicates that the surface reaches thermodynamic equilibrium under SR irradiation at temperatures much lower than that necessary for thermal desorption. For the 4° misoriented surface, nearly uniformly spaced and sized step bunches consisting of ~8 steps each were observed. The terrace edges were terminated along the boundaries of 7x7 unit cells in both cases of thermal and SR stimulated cleanings. These differences between 0° and 4° off samples are considered to be due to the difference of the migrating adatom densities, which strongly depend on step edge density.

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REFERENCES

[1] J. Takahashi, Y. Utsumi, H. Akazawa, I. Kawashima and T. Urisu, Appl. Phys. Lett. 58, 2776 (1991).

[2] H. Akazawa, Y. Utsumi, J. Takahashi and T. Urisu, Appl. Phys. Lett. 57, 2302 (1990).

[3] T. Urisu and H. Kyuragi, J. Vac. Sci. Technol. B 5, 1436 (1987).

[4] T. Miyamae, H. Uchida, I.H. Munro and T. Urisu, J. Vac. Sci. Technol. A 17, 1733 (1999).

[5] Y. Gao, H. Mekaru, T. Miyamae and T. Urisu, Appl. Phys. Lett. 76, 1392 (1999).

[6] Y. Gao, H. Mekaru, T. Miyamae and T. Urisu, J. Vac. Sci. A 18, 1153 (2000).

[7] X.-S. Wang, J.L. Goldberg, N.C. Bartelt, T.L. Einstein and E.D. Williams, Phys. Rev. Lett. 65, 2430 (1990).

[8] J.L. Goldberg, X.-S. Wang, J.Wei, N.C. Bartelt and E.D. Williams, J. Vac. Sci. Technol. A9, 1868 (1991).

[9] R. Trump, G.W. Rubloff, P. Balk, F.K. LeGoues and J. Van Loenen, Phys. Rev. Lett. 55, 2332 (1985).

[10] Y. Kobayashi and K. Sugii, J. Vac. Sci. Technol. A 10, 2308 (1992).

[11] H. Tochihara, W. Shimada, M. Itoh, H. Tanaka, M. Udagawa and I. Sumita, Phys. Rev. B 45, 11332 (1992).

[12] R.J. Phaneuf, E.D. Williams and N.C. Bartelt, Phys. Rev. B 38, 1984 (1988).

[13] B.S. Swartzentruber, Y.-W. Mo, M.B. Webb and M.G. Lagally, J. Vac. Sci. Technol. A7, 2901 (1989).

[14] H. Hibino, T. Fukuda, M. Suzuki, Y. Homma, T. Sato, M. Iwatsuki, K. Miki and H. Tokumoto, Phys. Rev. B 47, 13027 (1993).

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