PHYSICAL REVIEW B VOLUME 58, NUMBER 15 15 OCTOBER 1998-I

Influence of oxygen on the formation of Si(111)-7×7 domains studied by scanning tunneling microscopy

T. Ishimaru, T. Hoshino, H. Kawada, K. Shimada, T. Watanabe, and I. Ohdomari
School of Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan
and Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, 2-8-26 Nishiwaseda, Shinjuku-ku, Tokyo 169-0051, Japan

(Received 16 April 1998)

Coverage of the 7×7-reconstructed region on quenched Si(111) surfaces has been compared for two types of Si wafers with different oxygen concentration, Czochralski and modified float zone (m-FZ) wafers. The m-FZ wafer clearly showed the lower coverage, which suggested that oxygen had some influence on the formation of a 7×7 structure. The activation energy of formation of the 7×7 structure has been estimated to be 2.4 eV. [S0163-1829(98)01939-0]

I. INTRODUCTION

The Si(111)-7×7 DAS (dimer-adatom-stacking fault) reconstruction is one of the most studied subjects in semiconductor surface physics. Many results on dynamic features of nucleation and growth of the 7×7 domains have been reported by using reflection electron microscopy,[1] low energy electron reflection microscopy,[2] scanning tunneling microscopy (STM)[3,4] and so on. So far, it has been clarified that the 7×7 domains nucleate and grow preferentially at step edges, but they nucleate in terraces as well and grow in a triangular shape with the vertices pointing in $\langle \overline{1}\,\overline{1}2 \rangle$ directions. Our STM observation of the quenched surfaces at temperatures around 500 °C showed that stacking fault (SF) triangles were formed along a side of a triangular-shaped 7×7 domain,[5] and that a single SF triangle could be observed in the disordered 1×1 area.[6] From these results it has been concluded that a SF triangle is a building unit of the 7×7 domain.[5,6]

The dynamic aspects of the 7×7 formation, such as the behavior of atoms and the rate-determining process, however, have not been made clear yet. One of the authors (I. O.) proposed a model of $n\times n$ DAS structure formation,[7] in which he claimed that a flipping of the rest atoms bonded to oxygen atoms induced a conversion of 1×1 atomic configuration into a SF configuration in a cooperative manner, and that the formation of a SF triangle was completed by the in-phase merging of two SF regions. In his model, three oxygen atoms stabilize a corner hole, which otherwise stores high distortion energy and an unfaulted triangle is naturally formed by being surrounded by three SF triangles. The model is at least consistent with the experimental results of leading role of a SF triangle in nucleation, and growth of the 7×7 structure as mentioned above. Moreover, the incorporation of oxygen is very effective to stabilize the otherwise strained $n\times n$ DAS structure due to the strong bonding affinity between Si and oxygen.

The assumption made in the model that an $n\times n$ DAS half-unit contains three oxygen atoms has been very controversial. Recently Ueda reported, using time-of-flight type electron-stimulated desorption,[8] that a signal of oxygen was detected from the Si(111)7×7 surface in spite of no detection by the Auger electron spectroscopy method. Although this result does not necessarily support the above model of the oxygen-induced $1\times1\rightarrow7\times7$ phase transition, it is very interesting to know whether oxygen atoms are really responsible for the formation of the SF triangle or not.

In this work, we examine whether the formation of a 7×7 domain depends on the circumstances with different oxygen concentration. Upon quenching from a high temperature above that for the $1\times1\leftrightarrow7\times7$ phase transition, the Si(111) surface is partly covered with the 7×7 region because of the incomplete growth of the 7×7 domains.[9] In the present work, by taking full advantage of real-space observation with STM, coverage of Si(111) surfaces with the 7×7 phase has been measured for two types of samples of Czochralski (CZ) and modified float zone (FZ) (m-FZ) wafers containing different amounts of oxygen. The results clearly indicate the difference in coverage of the 7×7 region between them. We have also succeeded in the estimation of the activation energy for the 7×7 formation.

II. EXPERIMENT

All the experiments were performed in an UHV chamber with a base pressure of $<1\times10^{-10}$ mbar, equipped with a STM unit (JEOL 4000XV). Samples with a size of $7\times2\times0.3\ \text{mm}^3$ were cut from a CZ wafer with a resistivity of 8 Ω cm and an off angle of 0.5 ° and from a m-FZ wafer with the resistivity of 40 000 Ω cm and the off angle of 0.5 °. The m-FZ wafer was obtained by repetition of floating zone treatment many times in an UHV chamber to reduce the oxygen concentration. The oxygen concentrations in the CZ and m-FZ wafers were measured to be 6.4×10^{17} and 7.0×10^{15} atoms/cm^3, respectively by a radioactivation analysis. The lower oxygen concentration makes the m-FZ wafer more brittle than the CZ wafer, which might have some influence on the experimental result. Hence we measured the dislocation density by Sirtl-Anler etching method[10] to be $1.1\times10^{-2}\ \mu\text{m}^{-2}$ for m-FZ and $7.5\times10^{-3}\ \mu\text{m}^{-2}$ for CZ, respectively. These values mean that one dislocation is contained in the area of $10^2\ \mu\text{m}^2$, which is eventually zero in the $200\times200\text{-nm}^2$ region for STM observation. The areal density of dopants is so low for both CZ and m-FZ wafers

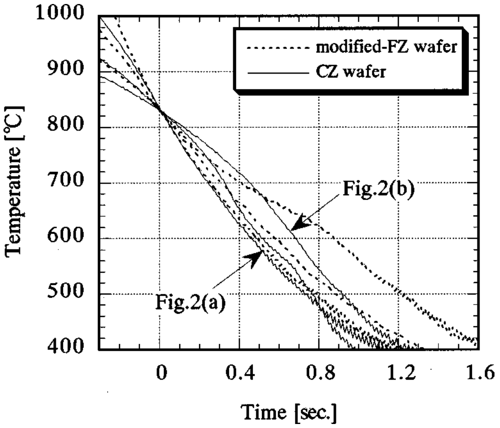

FIG. 1. Cooling curves during quenching. Solid and broken lines show cooling curves for CZ and m-FZ wafers, respectively. Each sample was quenched from 1100 °C to room temperature at three cooling rates.

that their influence on the $1\times1\rightarrow7\times7$ phase transition is negligible.

After organic chemical cleaning and 5% HF treatment, the samples were installed into the vacuum chamber, degassed at 500 °C for 12 h, and flashed up to 1200 °C. Preliminary STM observations were performed at room temperature to confirm that a whole area of the surfaces was covered with the 7×7 region after the flashing.

Quenching, from 1100 °C to room temperature, was carried out by shutting off the sample heater current or just by reducing the current. Substrate temperatures during quenching were monitored by an infrared pyrometer with quick response time of 1/1000 s and stored into a computer through an analog-to-digital converter at a rate of 1/100 s. After the quenching, STM observations to measure the 7×7 coverage were performed at room temperature with constant height mode and sample bias of -1 V. In order for reducing statistical fluctuation, the 7×7 coverage was determined from 50–60 STM images in each case.

III. RESULTS

Figure 1 shows the sample temperature changes during quenching. Each curve is drawn to start at $t=0$ at 830 °C, which is a typical critical temperature (T_c) of the $7\times7\leftrightarrow1\times1$ phase transition reported previously.[1,2] After quenching from 1100 °C to room temperature at three different cooling rates, we carried out all STM observations at room temperature at which the growth of the 7×7 domains do not proceed.

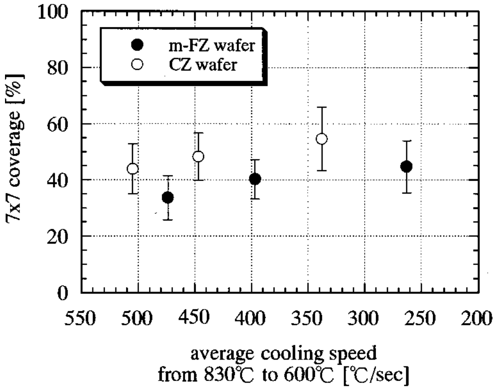

FIG. 3. 7×7 coverage on the surfaces of CZ-Si(111) (○) and the m-FZ-Si(111)(●) quenched with the different cooling curves. The length of the error bars shows the standard deviation.

Typical STM images (200×200 nm^2) of a surface of the CZ wafer quenched with the cooling curves indicated by the arrows in Fig. 1 are shown in Figs. 2(a) and 2(b). The average cooling speeds from 830 to 600 °C are 505 and 338 °C/s, respectively. The surfaces are partly covered with the triangular-shaped 7×7 domains. It should be noted that 7×7 domains grow larger on the surface quenched at the lower cooling rate. A magnified STM image of the regions where 7×7 domains did not grow shows that 2×2, $c2\times4$, and $c2\times8$ structures are formed, as reported previously.[11]

The 7×7 coverage for both samples of the m-FZ and CZ wafers quenched with three different cooling curves is shown in Fig. 3. The cooling speed is determined in the temperature range from the transition temperature $T_c=830$–600 °C, at which the 7×7 domains can still grow. A plot and an error bar indicate a mean coverage and the standard deviation, respectively. As clearly seen in Fig. 3, the 7×7 coverage for the m-FZ wafer is always lower than that of the CZ wafer. This result suggests that the 7×7 domains are easier to grow

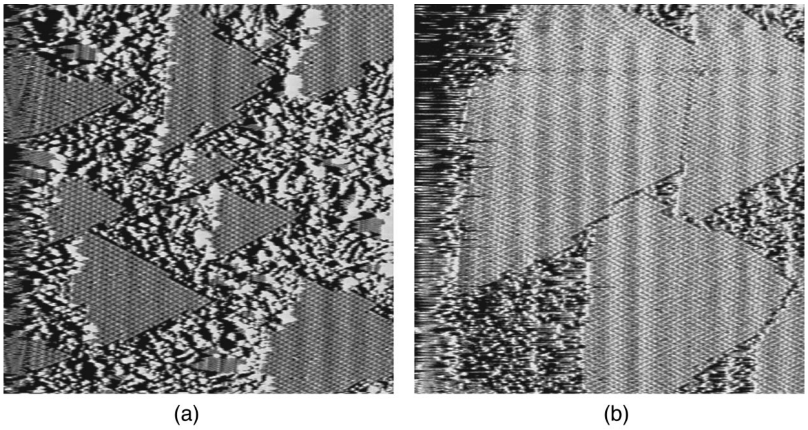
(a) (b)

FIG. 2. Typical STM images (200×200 nm^2) of CZ-Si(111) surface quenched with the cooling curves indicated by the arrows in Fig. 1. The graduations of the cooling curves from 830 to 600 °C are 505 °C/s and (b) 338 °C/s, respectively.

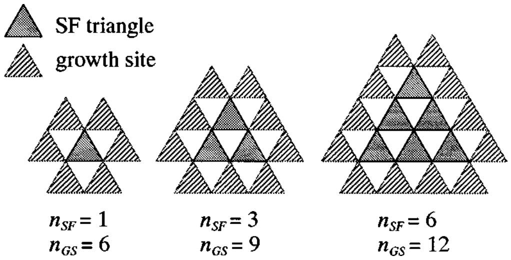

FIG. 4. A model of 7×7 domain growth used to estimate the activation energy for the 7×7 structure formation. It is based on our high-temperature STM observations of the growth of 7×7 domains (Refs. 5 and 9).

on the CZ wafer than on the m-FZ wafer. It also should be noted that the 7×7 coverage is always lower for larger temperature graduation for both the CZ and m-FZ wafers.

IV. DISCUSSION

Although an activation energy for the formation of 7×7 structure has hardly been determined yet so far, our present experiment enables us to deduce the value. Based on the experimental findings on the 7×7 domain growth obtained by our previous high-temperature STM observations,[5,9] and by taking advantage of the time-dependent feature of the 7×7 domain growth described above, the following growth model of the 7×7 region has been postulated. In the initial stage of nucleation, one 7×7 SF triangle is formed at first. Subsequently, the 7×7 domain grows in an equilateral triangular shape (Fig. 4) by adding new SF triangles with sharing a cornerhole.

The growth rate of the 7×7 domain can be considered to be proportional to the number of the formation sites for the additional 7×7 SF triangles. Since additional SF triangles should always share cornerholes with the original 7×7 domain, the equation of the 7×7 growth rate is expressed as follows by using the number of SF triangles contained in the 7×7 domain n_{SF}, the number of growth sites n_{GS}, and rate constant k:

$$\frac{dn_{SF}}{dt} = k n_{GS}. \tag{1}$$

From the equilateral triangular shape of the 7×7 domain, the relation between n_{SF} and the number of growth sites n_{GS} is given by

$$n_{GS} = \sqrt{18 n_{SF} + \tfrac{9}{4}} + \tfrac{3}{2}. \tag{2}$$

The rate constant k can be expressed by an Arrhenius-type equation.

$$k = A \exp\left(-\frac{E}{k_B T} \right), \tag{3}$$

where A is the frequency factor and E the activation energy. Integration of Eq. (1) gives

$$n_{SF} = \int_0^\infty n_{GS} A \exp\left(-\frac{E}{k_B T} \right) dt. \tag{4}$$

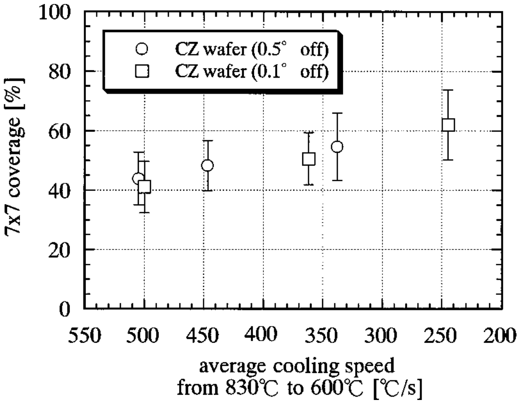

FIG. 5. 7×7 coverage on the CZ-Si(111) surfaces with different off angles. Circles and squares show coverages for wafers of 0.5° and 0.1°, respectively. There is no significant difference in the coverage.

Equation (4) gives the number of the SF triangles contained in the final 7×7 domain. The activation energy E can be determined so as to fit the left-hand side to the experimental value of the number of the 7×7 SF triangles contained in the average size 7×7 domain. Integration of Eq. (4) has been performed with a computer using the data of temperature change as measured in Fig. 1. The temperature range for the integration was set from 830 to 400 °C because the rate constant k at lower temperature below 400 °C is small enough to be neglected. The frequency factor A was assumed to be a general value of 10^{13}/s. The choice of 10^{12} as A cause only slight change in E in the order of 0.2 eV. The values of activation energy E obtained for the three quenching rates on the CZ wafer are almost the same, and have been estimated to be 2.4 eV. This value hardly changes in spite of variation in the 7×7 domain size. As for the m-FZ wafer, providing the frequency factor A is same as CZ wafer, the activation energy E becomes almost the same as that of CZ wafer.

Next we discuss the dominant activation process in the 1×1 →7×7 phase transition. Ohdomari's model suggests that the presence of oxygen is inevitable for the 7×7 structure, and that oxygen diffusion is essential for the formation of the 7×7 structure. A value of the activation energy of oxygen diffusion in Si crystal was reported to be 2.53 eV experimentally[12] and 2.43 eV theoretically.[13] Although the fact that the activation energy for the formation of the 7×7 structure obtained in this experiment is compatible with that of oxygen diffusion in Si crystal is not necessarily direct evidence of the oxygen-induced 7×7 formation, this is a very interesting coincidence. That is, the coincidence might suggest that oxygen diffusion in Si crystal is the rate-determining process of the 1×1 →7×7 phase transition. On the other hand, the diffusion process of a Si atom on a Si surface have been paid much attention with respect to the conversion from the 1×1 to 7×7 structure, because the atomic density of the 7×7 region is different from that of the 1×1 region.[14] The activation energy of Si-atom diffusion on a Si surface was reported in the range of 1.0–1.5 eV,[15–17] which is much lower than the value obtained in this experiment. If the diffusion process of a Si atom dominate the formation of the 7×7 structure, the growth of the 7×7 domain should become easier on the surface with a higher step density, because a step is the source of the Si-atom supply. Similar experiments using a CZ wafer with an off-angle of 0.1 ° have been carried out. The results are shown in Fig. 5 together with the results of a CZ wafer with an off-angle of 0.5 °. It is notable that the coverages of the two CZ wafers are almost the same. Therefore, it can be concluded that the diffusion process of a Si atom is not the rate-limiting process of the 7×7 structure formation. In this connection, it was pointed out previously that the $n\times n$ DAS structures can never be formed by chance as a result of a tremendous number of random walks of Si atoms.[18]

V. CONCLUSION

STM observations have been performed to study the influence of oxygen on the formation of the 7×7 domain. The 7×7 coverage on the surfaces of two kinds of Si(111) wafers, CZ-Si and m-FZ, with different oxygen concentrations, have been compared. The 7×7 coverage was lower for the m-FZ wafer with a lower oxygen concentration than for the CZ wafer with a higher oxygen concentration. The 7×7 coverage was smaller for the higher cooling rate upon quenching. By using the growth model of the 7×7 domain based on high-temperature STM observations, the formation of the 7×7 domain has been concluded to be a thermal activation process with an activation energy of 2.4 eV, which is much larger than the activation energy for Si surface migration.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Science and Culture, Japan, and by a Grant-in-Aid for the Research for the Future (RFTF) from the Japan Society for the Promotion of Science (JSPS). The authors are indebted to Dr. S. Hara of the Electrotechnical Laboratory for providing the CZ silicon wafer.

---

[1] N. Osakabe, Y. Tanishiro, K. Yagi, and G. Honjo, Surf. Sci. **109**, 353 (1981).

[2] W. Telieps and E. Bauer, Ultramicroscopy **1**, 57 (1985).

[3] S. Kitamura, T. Sato, and M. Iwatsuki, Nature (London) **351**, 215 (1991).

[4] K. Miki, Y. Morita, H. Tokumoto, T. Sato, M. Suzuki, and T. Fukuda, Ultramicroscopy **42-44**, 851 (1992).

[5] K. Kumamoto, T. Hoshino, K. Kokubun, T. Ishimaru, and I. Ohdomari, Phys. Rev. B **53**, 12 907 (1996).

[6] T. Hoshino, K. Kokubun, H. Fujiwara, K. Kumamoto, T. Ishimaru, and I. Ohdomari, Phys. Rev. Lett. **75**, 2372 (1995).

[7] I. Ohdomari, Surf. Sci. **271**, 170 (1992); Appl. Surf. Sci. **56-58**, 20 (1992).

[8] K. Ueda, Jpn. J. Appl. Phys. **34**, 248 (1995).

[9] T. Hoshino, K. Kumamoto, K. Kokubun, T. Ishimaru, and I. Ohdomari, Phys. Rev. B **51**, 14 594 (1995).

[10] E. Sirtl and A. Anler, Z. Metall. **52**, 529 (1961).

[11] T. Hoshino, K. Kokubun, K. Kumamoto, T. Ishimaru, and I. Ohdomari, Jpn. J. Appl. Phys. **34**, 3346 (1995).

[12] J. C. Mikkelsen, Jr., in *Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon*, edited by J. C. Mikkelsen, Jr., S. J. Pearton, J. W. Corbett, and S. J. Pennycook, MRS Symposia Proceedings No. 59 (Materials Research Society, Pittsburgh, 1986), p. 19.

[13] Z. Jiang and R. A. Brown, Phys. Rev. Lett. **74**, 2046 (1995).

[14] Y. N. Yang and E. D. Williams, Phys. Rev. Lett. **72**, 1862 (1994).

[15] R. F. C. Farrow, J. Electrochem. Soc. **121**, 899 (1974).

[16] E. Kasper, Appl. Phys. A: Solids Surf. **28**, 129 (1982).

[17] E. M. Pearson, T. Halicioglu, and W. A. Tiller, J. Cryst. Growth **83**, 499 (1987).

[18] I. Ohdomari, T. Watanabe, T. Hoshino, and K. Kumamoto, Phase Transit. **62**, 245 (1997).