Stability of the Dimer Structure Formed on Si(100) by Ultraclean Low-Pressure Chemical-Vapor Deposition

Stability of the dimer structure formed on Si(100) by ultraclean low-pressure chemical-vapor deposition

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Stability against air exposure of the dimer structure formed on Si(100) by ultraclean low-pressure chemical-vapor deposition was investigated. A 2×1-reconstructed dimer structure was clearly observed on the epitaxial Si film on Si(100) by reflection high-energy electron diffraction even after air exposure for 180 min. The dissociation process of the dimer structure and the oxidation process in the air depended on the cooling atmosphere in the reactor after chemical-vapor deposition as well as on the humidity of the air. It is proposed that the dissociation of the dimer structure in the air is suppressed by hydrogen adsorption and coincides with the oxidation of H-terminated or dangling bonds due to H_2O adsorption.

Si surface structure control is very important for the progress of atomic layer process to fabricate future Si devices. So far, ultrahigh vacuum has been widely used for investigations about surface structures.[1-3] On the other hand, since wafers are frequently exposed to the air between successive fabrication processes of devices, it is important to research the stability of the surface structure against air exposure. However, the observation of the surface structure in chemical-vapor deposition (CVD) or reactive ion etching (RIE), in which a high process pressure such as a few or a few hundred Pa is employed, has been scarcely reported. In this communication, we report the stability of the surface dimer structure formed on Si(100) by ultraclean low-pressure CVD (LPCVD) using SiH_4 and H_2, as well as the relationship between the dissociation process of the dimer structure and the oxidation process in the air.

The epitaxial Si film was grown on Si(100) for 30 min at 700 °C in SiH_4 and H_2 gas mixture using the ultraclean hot-wall LPCVD system.[4-6] The total and SiH_4 partial pressures during growth were about 17 and 2.6 Pa, respectively. After growing Si films, they were cooled down to a temperature below 50 °C in H_2 or Ar environment. The cooling time was about 90 min. As a reference, the wet-cleaned Si(100) surface was prepared by dipping into 2% HF solution for 30 s and rinsing with de-ionized water for 3 min. Also, the H_2 annealed Si(100) surface was prepared by annealing for 30 min at 700 °C and cooling for 90 min in H_2 in the LPCVD system. The surface structure was evaluated by reflection high-energy electron diffraction (RHEED) after exposing the surface to the air. The relative humidity (RH) levels of the air were 46%, 28%, and <1%. In the case of <1% RH (shown in Fig. 3), all the surfaces were exposed to the air of 46% RH for the first 5 min. The magnified views of the zeroth Laue zone in RHEED patterns were taken from the [011] azimuth. The incident angle of the electron beam was about 0.4°. The relative oxygen coverage on Si surfaces was evaluated from the intensity ratio of the SiO_x ($x \geqslant 0.5$) peak to the Si_{2p} peak in the x-ray photoelectron spectra (XPS).

Figure 1 shows the RHEED patterns of the CVD Si(100) surface cooled in H_2. The two-fold streaks are clearly observed, and the intensities of these two-fold streaks scarcely decrease even after air exposure for 180 min as shown in Figs. 1(a)–1(c). Similar two-fold streaks were also observed from the H_2 annealed Si(100) surface, even after exposing the surface to the air, although the wet-cleaned Si(100) surface showed a 1×1 streak pattern.
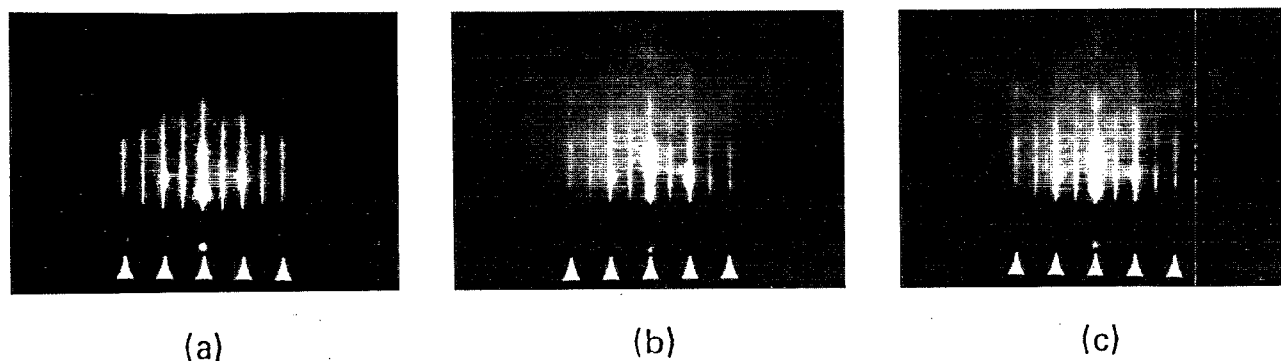

(a)   (b)   (c)

FIG. 1. Typical RHEED patterns from the CVD Si(100) surface after cooling in H_2 down to a temperature below 50 °C followed by exposure to the air of 28% RH for (a) 7, (b) 90, and (c) 180 min, respectively. The arrows show the positions of the fundamental 1×1 streaks.
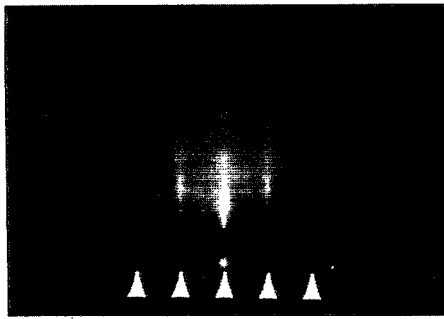
FIG. 2. Typical RHEED patterns from the CVD Si(100) surface after cooling in Ar down to a temperature below 50 °C followed by exposure to the air of 28% RH for 9 min. The arrows show the positions of the fundamental 1×1 streaks.

It is clear that the two-fold periodic arrangement of the dimer structure along the $[01\bar{1}]$ azimuth was formed by surface atom reconstruction, in other words, a 2×1-reconstructed surface with the dimer structure was formed.

When the CVD Si(100) surface was cooled in Ar from 700 to 450 °C and then in H_2 to a temperature below 50 °C, two-fold streaks similar to those shown in Fig. 1(a) were observed. However, the two-fold streaks gradually disappeared during air exposure, and became hardly observable after air exposure for 120 min. When the CVD Si(100) surface was cooled in Ar from 700 °C to a temperature below 50 °C and when the CVD Si(100) surface was cooled in Ar from 700 to 300 °C and then in H_2 to a temperature below 50 °C, the two-fold streak intensity had al-

ready weakened at the beginning of air exposure, as shown in Fig. 2. It is considered that the dissociation of the dimer structure in the air is suppressed by hydrogen adsorption on the surface, at least, in the temperature range above 450 °C.

In the cases mentioned above, the surfaces were exposed to the air of 28% RH. In the case of the air of 46% RH, the 2×1 streaks from the CVD Si(100) surface cooled in H_2 and from the H_2 annealed Si(100) surface disappeared after air exposure for 60 min, i.e., the stability of the dimer structure in the air strongly depends on the humidity of the air. Therefore, it is considered that the dissociation process of the dimer structure derives from H_2O adsorption on the surface.

Figure 3 shows the change of the XPS peak intensity ratio I_{SiO_x}/I_{Si} for various treated surfaces which were exposed to the air of 46% RH or RH below 1%. In the case of the CVD Si(100) surfaces, there is an apparent difference between Ar and H_2 as a cooling environment as shown in Figs. 3(a) and 3(b). The amount of oxygen on the CVD Si(100) surface cooled in Ar is relatively large ($I_{SiO_x}/I_{Si} = 0.1$–0.2). On the other hand, oxygen was scarcely observed on the CVD Si(100) surface cooled in H_2 for 60 minutes in the air of 46% RH and for 230 min in the air below 1% RH. In the case of H_2 annealed Si(100), the tendency of oxidation is similar to that of the CVD Si(100) surface cooled in H_2 as shown in Fig. 3(c). In the case of the wet-cleaned Si(100) surface, the relative oxygen coverage is constantly small for 200 min compared with the above surfaces as shown in Fig. 3(d). It is well
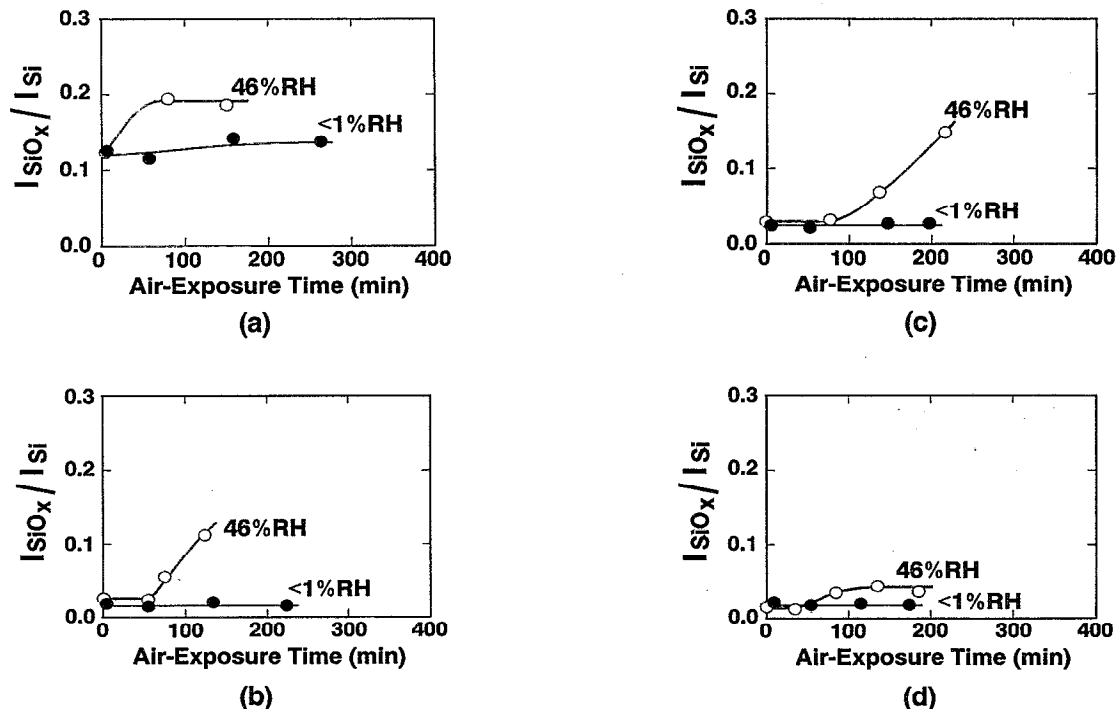

(a)

(c)

(b)

(d)

FIG. 3. Time dependencies of the XPS intensity ratio I_{SiO_x}/I_{Si} for various treated surfaces during exposure to the air of 46% RH or below 1% RH. The data was obtained after the surfaces were exposed to the air of 46% for 5 min. (a) CVD Si(100) surface cooled in Ar; (b) CVD Si(100) surface cooled in H_2; (c) H_2 annealed Si(100) surface cooled in H_2; (d) wet-cleaned Si(100) surface.

Sakuraba, Murota, and Ono

known that the wet-cleaned Si(100) surface is terminated by hydrogen, which causes suppression of oxidation.[7] Therefore, it is suggested that, in the cases shown in Figs. 3(b) and 3(c), the suppression of oxidation is caused from the hydrogen adsorption in a H_2 cooling environment. These results can be interpreted as the dimer structure dissociation due to surface oxidation.

In conclusion, a 2×1-reconstructed dimer structure was clearly observed on the epitaxial Si film on Si(100) by RHEED even after air exposure for 180 min. The dissociation process of the dimer structure in the air depended on the cooling atmosphere in the CVD reactor after deposition as well as on the humidity of the air to which the Si surfaces were exposed. The dissociation of the dimer structure in the air is suppressed by hydrogen adsorption and coincides with the oxidation of H-terminated or dangling bonds due to H_2O adsorption. Therefore, the dissociation of the dimer structure should be caused from the surface oxidation.

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Sakuraba, Murota, and Ono   3703