Stability of the Si(100) Surface Epitaxially Grown by CVD

Masao SAKURABA, Junichi MUROTA and Shoichi ONO

Laboratory for Microelectronics Research Institute of Electrical Communication Tohoku University 2-1-1 Katahira, Aoba-ku, Sendai 980, Japan

Stability against air exposure of the Si(100) surface epitaxially grown by CVD was investigated. A 2x1 reconstructed dimer structure was observed on the epitaxial Si film on Si(100) by RHEED even after air exposure for 180 minutes. The dissociation process of the dimer structure and the oxidation process in air depended on the cooling atmosphere in the CVD reactor after deposition as well as on the humidity of the air to which the film was exposed. The dissociation of the dimer structure in air is suppressed by hydrogen adsorption and coincides with the oxidation of H-terminated or dangling bonds due to H2O adsorption.

1. INTRODUCTION

Si surface structure control is very important for the progress of atomic layer process to fabricate future ULSI's. So far, ultrahigh vacuum has been widely used for investigations about surface structures¹⁾. Then, the observation of the surface structure in CVD or RIE process is difficult because of such a high process pressure as a few or a few hundreds Pa. On the other hand, wafers are frequently exposed to air between processes in the ULSI fabrication. Therefore, it is important to research the change of the surface structure by exposure to air. In this paper, we report a 2x1 reconstructed dimer structure of the Si(100) surface epitaxially grown by CVD using SiH4, which has been observed even after air exposure, as well as the relationship between dissociation process of the dimer structure and oxidation process in air.

2. EXPERIMENTAL

The epitaxial Si film was grown on Si(100) at 700°C for 30 minutes in a SiH4 and H2 gas mixture using an ultraclean hot-wall low-pressure CVD (LPCVD) system²⁻³⁾. After the growth, the Si film was cooled down to the temperature below 50°C in H2 or Ar environment. The cooling time was about 90 minutes. As a reference, the wet cleaned Si(100) surface was prepared by dipping into 2% HF solution for 30 seconds and DI water rinse for 3

minutes. Also, the H2 annealed Si(100) surface was prepared by annealing at 700°C for 30 minutes and cooling for 90 minutes in H2 in the LPCVD system. The surface structure was evaluated by RHEED after exposing the surfaces to the air. The relative humidity(RH) of the air was 46%, 28% or <1%. In the case of <1% RH, all the surfaces were exposed to the air of 46% RH or 26% RH for the first 5 minutes. The magnified views of the zeroth Laue zone in RHEED patterns were taken from the [011] azimuth. The incident angle of electron beam was about 0.4°. The relative oxygen coverage on the Si surface was evaluated by the intensity ratio of the $SiO_x(x>0.5)$ peak to the Si2p peak in the XPS spectra.

3. RESULTS AND DISCUSSION

Figure 1 shows the RHEED pattern of the CVD Si(100) surface cooled in H2. Additional streaks are observed in the middle of the fundamental 1x1 streaks, which means that the 2-fold periodic arrangement of the dimer structure in the $[01\overline{1}]$ azimuth is formed by surface atom reconstruction, in other words, a 2x1 reconstructed surface with the dimer structure is Intensities of these 2-fold streaks formed. scarcely decrease even after air exposure for 180 minutes as shown in Figs.1(a)-(c). Similar 2-fold streaks were observed from the H2 annealed Si(100) surface, although the wet cleaned Si surface showed an 1x1 streak pattern. It is considered that the dimer structure was formed by the hydrogen desorption.



Fig.1 Typical RHEED patterns from the CVD Si surface after cooling in H2 down to the temperature below 50° C followed by exposure to air of 28% RH for (a)7, (b)90, (c)180 minutes, respectively. The arrows show the positions of the fundamental 1x1 streaks.



Fig.2 Typical RHEED patterns from the CVD Si surface after cooling in Ar down to 450° C and in H2 down to the temperature below 50° C followed by exposure to the air of 28% RH for (a)9, (b)60 and (c)120 minutes, respectively. The arrows show the positions of the fundamental 1x1 streaks.

When the CVD Si surface was cooled in Ar from 700°C to 450°C and then in H2 from 450°C to the temperature below 50°C, the 2fold streaks similar to those shown in Fig.1(a) was observed (Fig.2(a)). However, the 2-fold streaks gradually disappears during air exposure (Fig.2(b)), and become hardly observable after air exposure for 120 minutes (Fig.2(c)). When the CVD Si surface was cooled in Ar from 700°C to the temperature below 50°C, the 2fold streaks have already weakened at the beginning of air exposure (Fig.3). It is clear that the dissociation of the dimer structure is enhanced by the hydrogen desorption.

In the cases mentioned above, the surface was exposed to the air of 28% RH. In the case of the air of 46% RH, the 2x1 streaks from the CVD Si surface cooled in H2 and from the H2 annealed Si surface disappeared after air exposure for 60 minutes. Thus, it is clear that the stability of the dimer structure in the air strongly depends on the humidity of the air, in other words, the dissociation process of the dimer structure derives from H2O adsorption on the surface.

In order to study the oxidation process of

.

Fig.3 Typical RHEED patterns from the CVD Si surface after cooling in Ar down to the temperature below 50° C followed by exposure to the air of 28% RH for 7 minutes. The arrows show the positions of the fundamental 1x1 streaks.

the CVD Si surface, the relative oxygen coverage on the Si surface was measured by Figure 4 shows the time dependence of XPS. the XPS peak intensity ratio ISiOx/ISi for various treated-surfaces during exposure to the air of 46% RH or below 1% RH. In the case of the CVD Si surface, there is an apparent difference between H2 and Ar as a cooling environment as shown in Figs.4(a) and (b). The adsorbed oxygen on the CVD Si surface cooled in Ar is relatively large (ISiOx/ISi=0.1-0.2). On the other hand, oxygen is scarcely adsorbed on the CVD Si surface cooled in H2 for 60 minutes in the air of 46% RH and for 230 minutes in the air below 1% RH. In the case of H2 annealed Si(100), the tendency of oxidation is similar to that of the CVD Si surface cooled in H2 as shown in Fig.4(c). In the case of the wet cleaned Si surface, the relative oxgen coverage is small and constant for 200 minutes as shown in Fig.4(d). It is well known that the wet cleaned surface is terminated by hydrogen, which causes suppression of oxidation⁴⁻⁵). Since hydrogen desorption from the Si surface during the cooling in Ar is considered to make the hydrogen coverage much lower than that of the CVD Si



(c) H2 annealed Si surface cooled in H2

(d) Wet cleaned Si surface

Fig.4 Time dependences of the XPS intensity ratio Isiox/Isi for various treated-surfaces during exposure to the air of 46% RH or below 1% RH. The data were obtained after the surfaces were exposed to the air of 46% RH for 5 minutes.

surface cooled in H2, different oxidation process shown in Fig.4 can be due to the difference of hydrogen adsorption. The dissociation process of the dimer structure shown in Figs.1-3 coincides with the oxidation process described above.

4. CONCLUSION

A 2x1 reconstructed dimer structure was observed on the epitaxial Si film on Si(100) by RHEED even after air exposure for 180 minutes. The dissociation process of the dimer structure in 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 surface was exposed. The dissociation of the dimer structure in air is suppressed by hydrogen adsorption and coincides with the oxidation of H-terminated or dangling bonds due to H2O adsorption.

ACKNOWLEDGEMENT

The authors wish to express their thanks to

Profs. Yasuji Sawada and Takashi Matsuura for their advice and encouragement in executing this study and to Mr. Takahiro Maeda and Mr. Yuushin Takasawa for their contributions to the CVD Si epitaxial growth experiments. The CVD reactor was produced by Kokusai Electric Co., Ltd. This study was carried out in the Superclean Room of the Laboratory for Micro-Research Institute of Electrical electronics, Communication, Tohoku University. This study was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

REFERENCES

- 1) Y.J.Chabal : J.Vac.Sci.Technol. A3 (1985) 1448.
- J.Murota et al. : Appl.Phys.Lett. 54 (1989) 1007.
- 3) J.Murota et al. : This conference.
- T.Takahagi et al. : J.Appl.Phys. 64 (1988) 3516.
- 5) M.Morita et al. : J.Appl.Phys. 68 (1990) 1272.

