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In-Situ Surface Cleaning Effect on Si Molecular Beam Epitaxy

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Rad clean process, a surface cleaning process for Si-MBE, using Si molecular beam radiation during pre-heat treatment, has been investigated in detail. Reduction of the etch pit densities in epitaxial Si films takes place because Rad clean process effectively eliminates oxide films from the surface of the substrates. The elimination of carbon on the surface, however, did not result simply in reduction of crystal defects.

Further, micro defect density strongly depends on the orientation of the substrates. This is an clear indication of the difference of growth mechanism between the orientation of (100) and (111).

1. Introduction

In molecular beam epitaxy (MBE), a crystal defect density in an epitaxial Si film strongly depends on residual contaminations at an initial epitaxial interface. To eliminate these defects from the MBE films, in-situ surface cleaning is always the most important process, and various methods have been reported, such as thermal treatment at high temperatures [1,2], Galliation [3], sputter cleaning [4], laser heating [5], Ozon pretreatment [6] and a-Si capping [7]. We have also reported the new surface cleaning method [8,9], Rad clean process which makes use of weak Si beam irradiation during pre-heat treatment. The process, based on etching/deposition condition on SiO_2 by weak Si beams [10], successfully reduced etch pit densities (EPDs) from the MBE Si films at enough low temperature of 700°C.

In the course of detailed investigation of Rad clean process, we examined the dependence of EPDs on the pre-heat time of Rad clean process, and residual oxygen and carbon at the initial interfaces, after Rad clean process had been performed, were also measured by SIMS. Further, to investigate the origins of micro defects formed during epitaxial growth [9], dependence of micro defects on the orientation of the substrates was also studied.

2. Experimental Procedure

CZ-76mmϕ (111) Si substrates, either P or N type, were used in these experiments. (100) substrates were also used only for the experiment of the dependence on the orientation. Thin natural oxide films of about 1.2 nm covered the substrates after being boiled in NH_4OH/H_2O_2 and rinsed in ultra pure water. Immediately after the cleaning, they were charged into the ultra high vacuum MBE chamber. The natural oxide films were removed by Rad clean process in various conditions under the pressure of less than 1×10^{-9} Torr, and successively, about 0.5 μm thick epitaxial films were grown at about 0.6 nm/sec.

For the measurement of the substrate temperature and the growth rate (Si beam intensity), infrared optical pyrometer and quartz oscillator thickness monitors were used, respectively. And to realize the stable weak Si molecular beams, also for controlling supplied power of E-gun for the Si molecular beam source, the beam was cut to 1/5 by periodically closing a shutter every few seconds.

To evaluate the crystal defects in the epitaxial films, micro defects were delineated by Sirtl etching and EPDs were counted by using optical microscope of ×400 and ×1,000, and also detailed observation of the etched surface were performed by SEM. And to confirm the origin of the crystal defects, depth profiles of oxygen and carbon were measured by SIMS using primary Cs^+ ion.

3. Results and Discussion

Figure 1 shows the relation of EPDs and pre-heat time of Rad clean process at various temperatures. Si beam intensities were about $3\times10^{14}/cm^2/sec$ at 800°C, and in other cases about $3\times10^{13}/cm^2/sec$. The figure indicates that at 750°C and 700°C, longer pre-heat periods are required to reduce EPDs than that at 800°C, because the etching rates at these temperatures are very low. The etching rate at 700°C of about 0.15 nm/min is lower than that at 750°C of about 0.25 nm/min with the same Si beam intensity that is far below the critical beam intensity at 700°C [10]. It is suggested that the etching rate of the oxide film depends not only on the Si beam intensity but also on the pre-heat temperature.

On the other hand, at 650°C, EPD reduction is not observed at all, because the Si beam intensity is too strong to etch off the oxide, instead Si deposition on the oxide predominantly takes place.

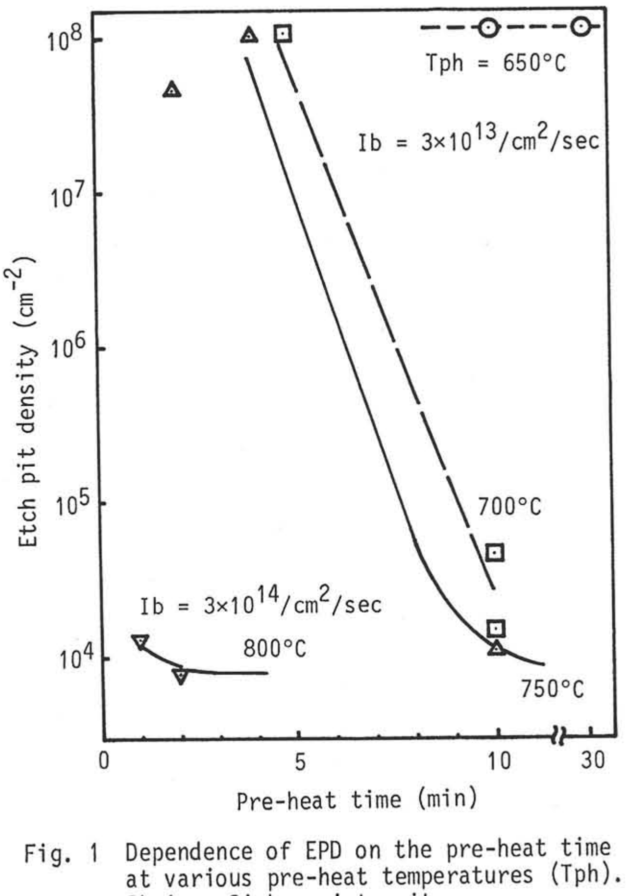

Fig. 1 Dependence of EPD on the pre-heat time at various pre-heat temperatures (Tph). Ib is a Si beam intensity.

Figure 2 shows the depth profiles of oxygen and carbon measured by SIMS at the pre-heat temperature of 750°C and at the Si beam intensity of $3\times10^{13}/cm^2/sec$. The interfacial excess oxygen peak, observed at the pre-heat time of 2 min, disappeared by longer pre-heat of 10 min. This confirms that the natural oxide films are effectively etched by Rad clean process at the pre-heat temperature of 750°C. We have also confirmed by the SIMS analysis that even at 700°C and at 800°C the oxide films were removed by Rad clean process, and that the oxide film could not be removed at 650°C even after a long pre-heat time.

On the other hand, interfacial excess carbon peaks were still observed even after a long pre-heat time of 10 min, not only as shown in Fig. 2 but also in a lot of measured carbon profiles in these experiments. This fact is a clear indication that Rad clean process can not remove carbon from the surface of the substrates. We have already found that these carbon contamination is formed during NH_4OH/H_2O_2 cleaning process.

The dependence of EPDs on the peak top concentrations of interfacial oxygen and carbon was examined in Fig. 3, in which open squares corre-

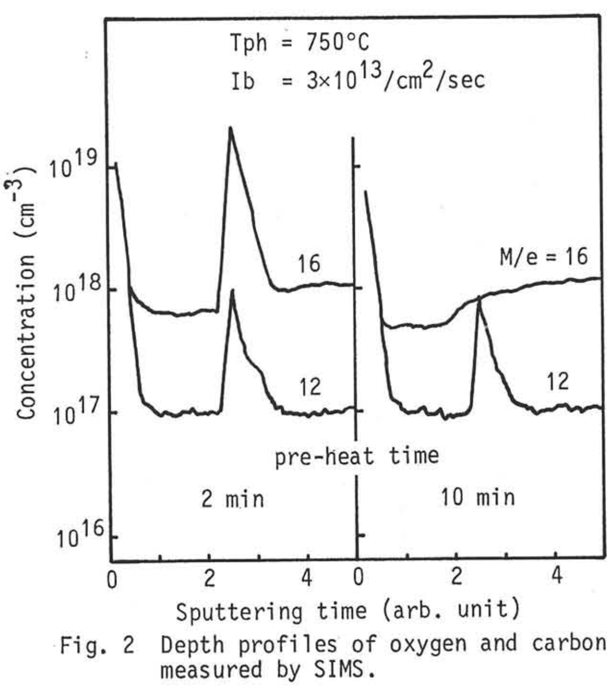

Fig. 2 Depth profiles of oxygen and carbon measured by SIMS.

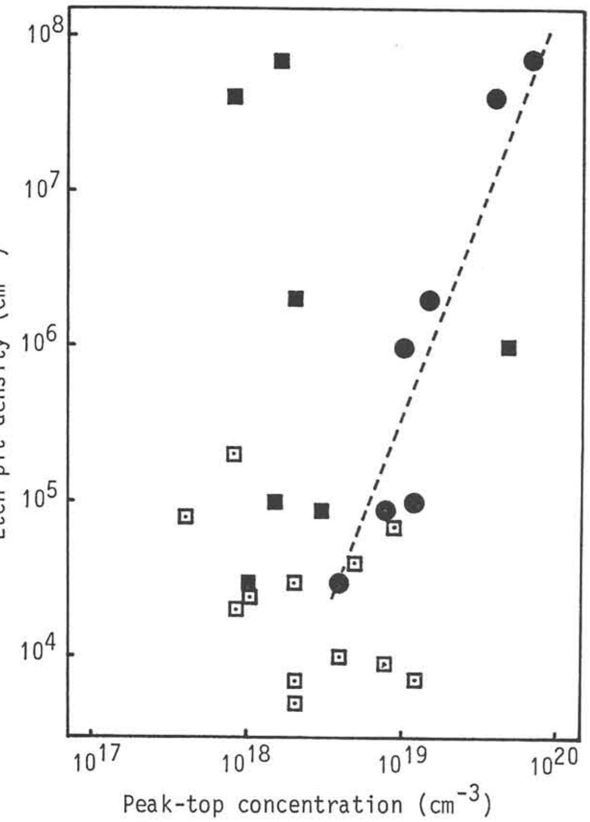

Fig. 3 Relation between EPD and peak top concentration of the interfacial oxygen (●) and carbon (□ ■).

spond to carbon when no interfacial excess oxygen peaks are observed, and solid circles and squares correspond to oxygen and carbon, respectively, when interfacial excess oxygen peaks are observed. It is clear that the EPDs strongly depend on the amounts of the interfacial oxygen, but when no interfacial excess oxygen peaks exist, EPDs, remaining still of the order of $10^3/cm^2$, were not clearly corelated to the amount of the interfacial carbon.

These SIMS analysis suggests that EPDs are mainly due to the interfacial excess oxygen, that even if no excess oxygen exists at the interface, however, residual EPDs of the order of $10^3/cm^2$ were still observed and that the amount of the interfacial carbon did not simply result in the EPDs.

To reveal another origins of the residual EPDs besides the interfacial carbon, dependence of EPDs and micro defects on the substrate orientation were investigated. Though EPDs on (100) oriented substrates were too small to be counted accurately, generally they are more than 10^2 order smaller than those or (111) oriented substrates even if the large interfacial carbon peaks were observed. Figure 4 shows the SEM photographs of the Sirtl etched MBE Si films grown on (100) and (111) oriented Si substrates. The films were grown at 650°C after 2 min Rad clean process at 800°C and Si molecular beam intensity of about $3\times10^{14}/cm^2/sec$.

There are no specific features at (100), however, a lot of triangle shaped micro defects of about 0.2 μm in length, are observed at (111). As these micro defects were assumed to be formed during the epitaxial growth [9], epitaxial growth on (111) oriented substrate has some difficulties compared to that on (100) substrate. It is not yet clear whether this is due to the incorporation of the contaminations from the atmosphere or due to the growth mechanism itself.

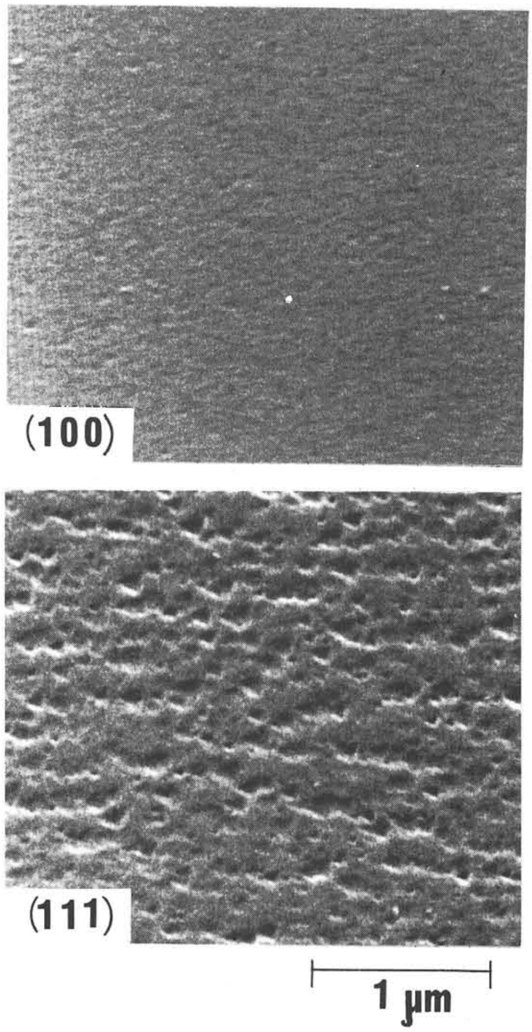

Fig. 4 SEM photographs of Sirtl etched surfaces of MBE films on (100) and (111) oriented substrates.

4. Conclusion

The SIMS analysis revealed that the crystal defects represented by EPD depend primarily on the amount of interfacial excess oxygen, and that the elimination of carbon at the interface did not simply result in the reduction of EPD. Crystal defects also strongly depend on the substrate orientation, and micro defects were not observed on (100) substrates but on (111) substrates. To reduce crystal defects from the MBE films on (111) substrates, the detailed mechanism of the epitaxial growth should be counted on.

It has also been proved that Rad clean process can effectively remove the natural oxide films formed during NH_4OH/H_2O_2 cleaning process, even at low temperature of 700°C. Further investigation is necessary to make clear the effect of Rad clean process precisely, such as the role of Si molecular beam.

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References

(1) A. Kimura; Solid-State Electron. 48 (1975) 901.

(2) H. Sugiura and M. Yamaguchi; J. Vac. Sci. Tech. 23 (1981) 18.

(3) S. Wright and H. Kroemer; Appl. Phys. Lett. 36 (1980) 210.

(4) J.C. Bean, G.E. Becker, P.M. Petroff and T.E. Seidel; J. Appl. Phys. 48 (1977) 907.

(5) T. De Jong, L. Smit, V.V. Korablev and F.V. Saris; Laser and Elect.-Beam Interact. with Solid (1982), Vol.4, Part 2, p.215.

(6) M. Tabe and K. Kajiyama; Abst. of the 31st Spring Meet. of the Japan Soc. Appl. Phys. and of the Related Soc., Tokyo, March 1984.

(7) B.A. Joice, R.R. Bradley and G.R. Booker; Phil. Mag. 15 (1967) 1167.

(8) N. Matsuo, Y. Hirofuji and K. Kugimiya; Ext. Abst. of the 16th Conf. on Solid-State Dev. and Mat., (1984) 56.

(9) K. Kugimiya, Y. Hirofuji and N. Matsuo; Jpn. J. Appl. Phys., 24 (1985) 564.

(10) M. Tabe; Jpn. J. Appl. Phys., 21 (1982) 534.