Electron-cyclotron-resonance plasma-enhanced chemical vapor deposition of epitaxial Si without substrate heating by ultraclean processing

著者	室田　淳一
journal or publication title	Applied Physics Letters
volume	59
number	22
page range	2853-2855
year	1991
URL	http://hdl.handle.net/10097/47683

doi: 10.1063/1.105855

Electron-cyclotron-resonance plasma-enhanced chemical vapor deposition of epitaxial Si without substrate heating by ultraclean processing

Koichi Fukuda,[a] Junichi Murota, and Shoichi Ono
Research Institute of Electrical Communication, Tohoku University, Katahira, Sendai 980, Japan

Takashi Matsuura, Hiroaki Uetake,[b] and Tadahiro Ohmi
Department of Electronics, Faculty of Engineering, Tohoku University, Aramaki, Sendai 980, Japan

(Received 1 July 1991; accepted for publication 29 August 1991)

By Ar plasma-enhanced decomposition of SiH_4 using ultraclean electron-cyclotron-resonance plasma processing, low-temperature Si epitaxy has been achieved even without external substrate heating for the first time. Ar plasma pre-exposure experiments have revealed that Ar ion energies lower than a few eV are favorable for Si epitaxy at low temperatures, in order to suppress plasma damage on the surface crystallinity. Furthermore, it has been found that addition of H_2 to the Ar plasma is extremely effective to remove the native oxide layer on the Si surface.

Lowering the Si epitaxial temperature is important for manufacturing future semiconductor devices. Although Si epitaxy at a temperature as low as 120 °C has been performed by the molecular beam epitaxy method, it was necessary to heat the sample up to 1200 °C before deposition for cleaning its surface.[1] By a conventional plasma chemical vapor deposition (CVD) method[2] and by a remote plasma-enhanced CVD method,[3] Si epitaxial growth was performed at temperatures as low as 230 and 150 °C, respectively. So far, external substrate heating by an electrical heater, etc., has been necessary to achieve Si epitaxy. In plasma processing for epitaxy, conditions of plasma (e.g., energy of ions) must be optimized in order to suppress plasma damage, because the quality of deposited films depends on damage and the thermal recovery of damage is less at lower temperatures. Since the energy of ions in an electron-cyclotron-resonance (ECR) plasma system is comparatively low,[4] ECR plasma processing is considered to be advantageous for low-temperature Si epitaxy. However, the reported epitaxial temperature in ECR-type reactive ion beam deposition was $T \geqslant 400$ °C.[5] It is well known that contaminants such as water molecules are adsorbed on the wafer surface more easily, and as a result, epitaxy becomes more difficult at lower temperatures. In low-temperature epitaxial processing, therefore, it is also important to reduce contamination.

In the present work, by ultraclean ECR plasma processing, low-temperature Si epitaxy without external substrate heating has been realized for the first time. Effects of plasma damage on the epitaxial growth are studied. Furthermore, surface cleaning by plasma is investigated using samples with native oxides formed intentionally on the surface.

The ultraclean ECR plasma apparatus used is schematically shown in Fig. 1.[6] The ultimate vacuum of the chamber exhausted by an oil-free turbo molecular pumping (TMP) system was about 5×10^{-9} Torr. The wafer susceptor was not heated externally at all. SiH_4 gas was supplied into the deposition chamber, which was separated from the plasma generating chamber by a plate with a window of 100 mm diameter. Ar and H_2 gases were introduced into the plasma generating chamber, and the generated ions were carried to the wafer through a divergent magnetic field without using an ion extraction electrode. All gases used are of ultraclean grade.[7]

The substrates used were *p*-type Si wafers of 3–8 Ω cm with mirror-polished (100) surfaces and with patterned thermal SiO_2 films. After cleaning in several cycles in a 4:1 solution of H_2SO_4 and H_2O_2, and DI water, the samples were treated in diluted HF and rinsed with DI water just before loading into the ECR chamber. Only in the case to investigate the surface cleaning by plasma pre-exposure, native oxides were intentionally formed on the sample surface by an additional treatment in a H_2SO_4-H_2O_2 solution followed by rinsing with DI water.

The following deposition conditions were chosen: the microwave (2.45 GHz) power was 700 W, the wafer was at a floating potential, the deposition time was 40 min, the SiH_4 partial pressure was 3×10^{-6} Torr, the Ar pressure was 6×10^{-3} Torr, and H_2 was not added during deposi-

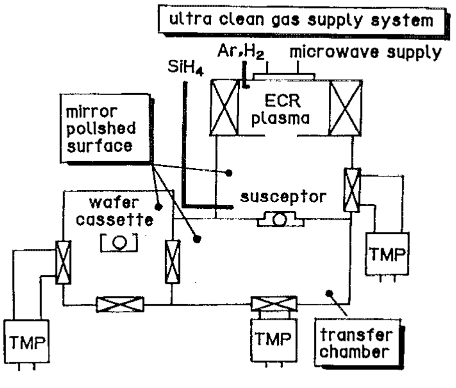
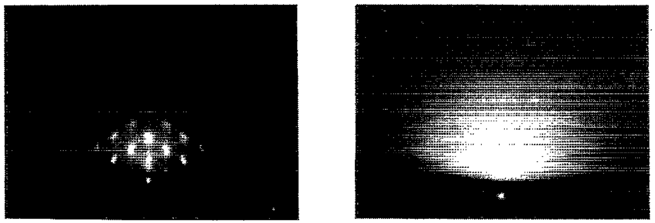


FIG. 1. Schematical diagram of the ultraclean ECR plasma apparatus. SiH_4 gas is introduced into the deposition chamber. Ar and H_2 gases are introduced into the plasma generating chamber.

---

[a] On leave from Alps Electric Co., Ltd., Izumi-ku, Sendai 981-11, Japan.
[b] On leave from Seiko Instruments Inc., Matsudo, Chiba 271, Japan.



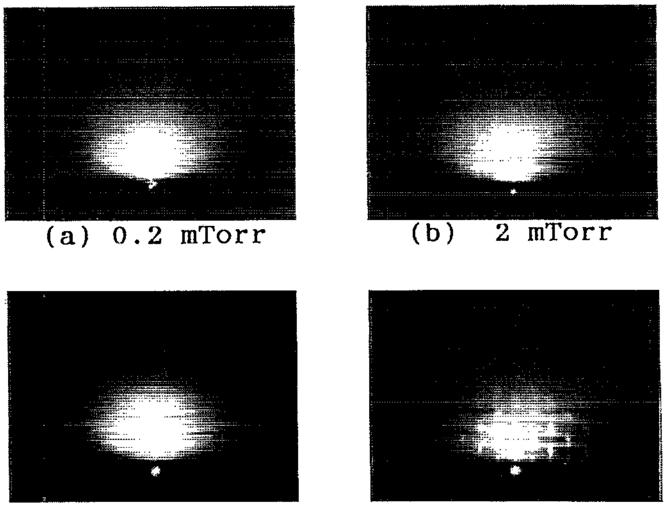
(a) on Si (b) on SiO_2

FIG. 2. Typical electron diffraction patterns for Si films deposited on (a) Si and (b) SiO_2 without plasma pre-exposure.

tion. These gas pressures were selected in order to suppress the reversal flow of SiH_4 into the plasma generating chamber which causes Si deposition on the quartz window for microwave introduction. The deposited film thickness under these conditions was about 600 Å, which was measured by Tencor Alpha Step with a partial removal of the deposited films by wet chemical etching. To investigate the effects of plasma pre-exposure on the structure of deposited films, substrates were exposed to a pure Ar plasma and an Ar plasma with 10% H_2 addition, just before the film deposition. The structure of the films was evaluated by electron diffraction (ED) with the [011] direction of electron incidence.

Si films were deposited both on Si and SiO_2. Figure 2 shows the typical ED patterns of the films deposited without plasma pre-exposure. The pattern of the film on Si shows Laue reflections which indicates single crystallinity, whereas the pattern on SiO_2 shows halo, indicating an amorphous film. Here, it should be noted that, without substrate heating, the surface temperature of substrates was 25 °C just before the deposition, and during the deposition it was elevated up to ~200 °C, which was estimated by change after the plasma turning off in *I-V* characteristics of *pn* diodes previously formed on the wafer surface. The present low-temperature epitaxy without substrate heating is considered to be due to the ultraclean processing.

Since there should exist the optimum ion energy for epitaxy, at which surface reaction/migration is enhanced while plasma damage is minimized,[8] the effects of plasma damage on the crystallinity of deposited films were examined by the wafer pre-exposure to an Ar plasma. The results are shown in Fig. 3. For the higher Ar pressure (2–20 mTorr), epitaxial growth is observed, especially, the best crystal quality indicated by a streaky pattern is obtained at 6 mTorr, while for a lower pressure (0.2 mTorr) amorphous films are grown. Since it is known that the typical peak energy of ions in the ECR system is a few 10's eV at 0.2 mTorr, and lower than a few eV at higher pressures than 2 mTorr,[9,10] which is a comparable order of magnitude to the Si—Si bond energy of 2.4 eV in bulk Si.[11] Therefore, the above facts should be understood as follows: Low-energy ions at a high pressure such as 6 mTorr cause so little damage that Si epitaxial films can be grown without substrate heating, whereas high-energy ions at 0.2 mTorr cause damage of the surface crystallinity. It was reported that Si epitaxial growth was observed at 630 °C under high ion energy conditions at about 0.2 mTorr in a conventional ECR system.[12] Thus, it is considered that effects of damage on Si epitaxy are larger at lower temperatures because of a decrease in the thermal recovery of damage. Consequently, it is necessary to lower the ion energy for epitaxy at low temperatures.

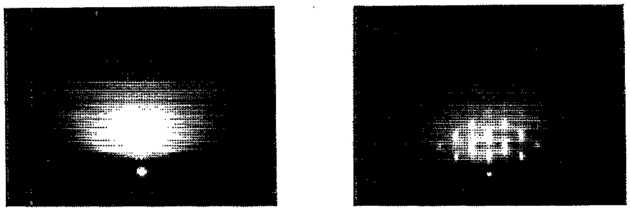


(a) 0.2 mTorr (b) 2 mTorr

(c) 6 mTorr (d) 20 mTorr

FIG. 3. Electron diffraction patterns for Si films deposited after the pre-exposure of the sample for 150 s to an Ar plasma with a pressure of (a) 0.2 mTorr, (b) 2 mTorr, (c) 6 mTorr, and (d) 20 mTorr, and a microwave power of 700 W.

Surface cleaning effects by plasma were investigated using wafers with native oxides formed intentionally on the surface. Figure 4 compares the ED patterns of samples pre-exposed to (a) pure and (b) H_2 added Ar plasmas, followed by the deposition under the same condition. Although the halo pattern is obtained in the case of pure Ar plasma pre-exposure, Laue spots are observed in the case of pre-exposure to H_2 added Ar plasma for a time of only 15 s. Thus, the hydrogen addition is very effective to remove the native oxides on the surface. The dependence of crystallinity on the cleaning plasma pressure was also investigated. Cleaning by a 10% H_2 added Ar plasma at pressures of 2 and 6 mTorr for only 15 s was sufficient to remove the native oxide and to obtain epitaxial growth. The amorphous pattern was obtained at 0.2 mTorr and the



(a) pure Ar (b) 10 % H_2 added Ar

FIG. 4. Electron diffraction patterns for Si films deposited on the substrates with native oxides after the pre-exposure of the sample for 15 s to (a) a pure Ar plasma and (b) a 10% addition of H_2 to the Ar plasma, with a total pressure of 6 mTorr and a microwave power of 300 W.

amorphous/polycrystal-like pattern was observed with less reproducibility at 20 mTorr, both of which indicated insufficient cleaning. Si surface cleaning by ECR H_2 plasma for GaAs heteroepitaxy on Si has been reported.[13] However, the typical cleaning conditions were different from those of the present one, that is, a cleaning temperature of 400 °C, a gas pressure of 0.2 mTorr, and a cleaning time of 20–30 min. The present results show that a clean Si surface can be obtained by the ultraclean ECR plasma exposure at a much lower temperature, at a much higher pressure around 2–6 mTorr with lower ion energies, and for a much shorter cleaning time.

In conclusion, low-temperature Si epitaxy without substrate heating was realized under low ion energies, i.e., damage-suppressing conditions, by the ultraclean ECR plasma-enhanced decomposition of SiH_4. Exposure to H_2-added Ar plasma is extremely effective to achieve a clean Si surface at very low temperatures.

The authors greatly acknowledge Professor N. Mikoshiba for encouragments throughout this study. They also thank T. Kawashima and Y. Yamashita, Seiko Instruments Inc., for manufacturing the ultraclean ECR apparatus, and S. Matsuo, NTT, for valuable advice about apparatus. This study was carried out in the Superclean Room of the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University. This study was partially supported by Grant-in-Aid for Developmental Scientific Research, Ministry of Education, Japan (03555057).

[1] Y. Shiraki, Y. Katayama, K. L. I. Kobayashi, and K. F. Komatsubara, J. Cryst. Growth **45**, 287 (1978).

[2] T. Uematsu, S. Matsubara, M. Kondo, M. Tamura, and T. Saitoh, Jpn. J. Appl. Phys. **27**, L493 (1988).

[3] L. Breaux, B. Anthony, T. Hsu, S. Banerjee, and A. Tasch, Appl. Phys. Lett. **55**, 1885 (1989).

[4] T. Ono, M. Oda, C. Takahashi, and S. Matsuo, J. Vac. Sci. Technol. B **4**, 696 (1986).

[5] H. Yamada and Y. Torii, Extended Abstracts 17th Conference on Solid State Devices and Materials, Tokyo, 1985, Jpn Society of Appl. Phys., Tokyo, 1985, p. 305.

[6] T. Matsuura, H. Uetake, T. Ohmi, J. Murota, K. Fukuda, N. Mikoshiba, T. Kawashima, and Y. Yamashita, Appl. Phys. Lett. **56**, 1339 (1990).

[7] T. Ohmi, J. Murota, Y. Kanno, Y. Mitsui, K. Sugiyama, T. Kawasaki, and H. Kawano, in *USLI Science and Technology 1987*, edited by S. Broydo and C. M. Osburn (Electrochemical Society, Pennington, 1987), p. 805.

[8] T. Ohmi, T. Ichikawa, T. Shibata, K. Matsudo, and H. Iwabuchi, Appl. Phys. Lett. **53**, 45 (1988).

[9] K. Nishioka, N. Fujiwara, M. Yoneda, and T. Kato, Microelectron. Eng. **9**, 481 (1989).

[10] M. Matsuoka and K. Ono, J. Vac. Sci. Technol. A **6**, 25 (1988).

[11] Calculated using the data in *CRC Handbook of Chemistry and Physics*, 70th edition, edited by R. C. Weast (CRC, Boca Raton, 1989), p. D-83.

[12] I. Nagai, T. Takahagi, A. Ishitani, H. Kuroda, and M. Yoshikawa, J. Appl. Phys. **64**, 5183 (1988).

[13] T. Shibata, Y. Nanishi, and M. Fujimoto, Jpn. J. Appl. Phys. **29**, L1181 (1990).