Surface Reaction Film Formation by Si₂H₆ Transfer at Molecular Flow

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ABSTRACT

High-rate silicon epitaxial growth of 1.1 μ m/min has been achieved at a substrate temperature of 750°C by using a new source gas supply system, such as a free-jet molecular flow expanding into ultra-high vacuum. Film formation is thought to be carried out by the surface reaction of adsorbed source gas molecules, without production of microparticles by any accompanying vapor phase reaction, which would degrade film qualities. It was found that the effect of electron-hole excitation in the substrate with a xenon lamp is also involved in the high-rate growth. The newly developed system is cleaning-free, because there is no deposition of reaction by-products on the inner surface of the chamber wall.

In the chemical vapor deposition (CVD) which is widely used for the formation of various thin films, particularly in the very large scale integration (VLSI) process technologies, the source gases exhibit a viscous flow, in which a stagnant layer is inevitably formed on the substrate surface, due to thermal convection above the heating susceptor (1). The source gas molecules are supplied to the substrate surface by density diffusion through the stagnant layer. In this conventional deposition process, the vapor phase reaction has been minimized by varying the process parameters. However, a film formation system which suppresses the vapor phase reaction without optimizing the process parameters has not been constructed so far. The vapor phase reaction of source gas molecules results in the creation of microparticles which degrade the film quality, and in the deposition of large amounts of chemical byproducts on the inner surface of the chamber wall. The excess molecules are wasted, increasing the energy spent on fume-scrubbing in the exhaust system. The incessant manual cleaning, to eliminate the by-products from the inner surface of the chamber wall, has been really carried out in the VLSI production line. This cleaning procedure causes a decrease in the running time of the fabricating machine, and degradation of the environment cleanliness in the chamber, because the chamber wall is contaminated by air, particularly moisture molecules, whenever the cleaning procedure is performed. Thus, conventional CVD includes serious disadvantages. In this paper we describe a novel film formation technology, using free-jet molecular flow, which is characterized by film formation through surface reactions without accompanying vapor phase reactions. The new technology maintains cleanliness in the reaction chamber during and after the film formation (2-4). The enhancement of the growth rate by electron-hole excitation in the substrate with a xenon (Xe) lamp is also demonstrated.

Experimental

The schematic diagram of the newly developed film formation system is illustrated in Fig. 1. The inner surface of the stainless steel chamber is coated with a corrosionresistant layer of TiN. The reaction chamber is always pumped down with a turbo molecular pump (2000 1/s) to pressures of less than 1×10^{-8} torr. The high vacuum system makes possible the immediate elimination of chemical by-products from the substrate surface, due to the long mean free path of these molecules. The Si substrate was set face-up on the susceptor by the loadlock system with the electrostatic wafer chuck. The substrate on the TiNcoated stainless steel or on the SiC-coated carbon susceptor was preferentially heated by the irradiation of the collimated light of a Xe lamp, which had been set above the Si substrate (surface irradiation), or two Xe lamps (surface and back side irradiation), or infrared (IR) lamps (surface irradiation). The susceptor temperature was monitored by a thermocouple buried in it. The substrate temperature was calibrated by measuring with a thermocouple attached to the substrate under the same condition as the growth. An ultra-clean source gas (Si₂H₆) was introduced into the chamber through the ultra-clean gas delivery system (5, 6). The source gas was directly supplied at high velocity onto the substrate surface, through a gas nozzle having a diameter of 500 μ m and a length of 1 mm.

The substrates were B-doped (100) and (111) Si wafers having a diameter of 50 mm. The Si substrates were chemically cleaned, and ultra-pure water, with dissolved oxygen below 600 ppb, was used for final rinse of the Si substrates. This dissolved oxygen concentration mainly comes from oxygen diffusion from the air to the final rinsing vessel, because the dissolved oxygen concentration is reduced to 40 ppb in the ultra-pure deionized water system. Native oxide growth is suppressed within 10³ min on the Si surface, except the highly doped n⁺ layer, while the dissolved oxygen concentration is kept at 600 ppb in ultra-pure water (7, 8). The Si substrate surface was dried by hot, clean Ar gas blowing, before film formation. The SiO₂ (~100 nm)/Si substrates were produced by thermal oxidation of Si substrates. To determine the grown film thickness, Si substrates on which SiO₂ layers were patterned like stripes were also used. The thicknesses of the grown films formed on the stripe substrates were determined by etching any area of the polycrystalline Si on SiO2 layers, and by using the surface profiler. The film formation was carried out at temperatures between 550° and 750°C. Some substrates were heated on the stainless steel susceptor using IR lamps, and the other substrates were heated on the carbon susceptor using the xenon lamp. The flow rates of Si₂H₆



Fig. 1. Film formation system

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Fig. 2. Flow rate dependence of epitaxial rate for Xe lamp irradiation, and growth efficiency, which is defined as a ratio of the number of Si atoms in the growth film to that in the source gas supplied during the growth.

gas were varied from 10 to 100 standard cubic centimeters per minute (sccm). The pressure near the chamber inner surface was approximately 10^{-3} torr during the film formation. The crystallographic structure of Si films was evaluated by reflective electron diffraction. The surface morphology of the as-deposited films was observed by Normarsky interference optical microscope, and the surface morphology of Wright etched films was observed by scanning electron microscope.

Results and Discussion

Figure 2 shows the flow rate dependence of the epitaxial growth rate for the surface and back side irradiation by Xe lamps, and growth efficiency, which is defined as a ratio of the number of Si atoms in the grown film to that in the source gas supplied during the growth. High-rate growth (1.1 μ m/min or higher) has been obtained at the substrate temperature of 750°C for 100 sccm. This results from the thermal instability of the Si₂H₆ molecule, the high-speed molecular flow expanding onto the substrate surface, and the fast elimination of by-products from the substrate surface.

The flow rate dependence of growth rate on the Si (100) substrates and the SiO₂/Si substrates, for the substrate temperatures as a parameter, are shown in Fig. 3 and 4, respectively, where the substrates were heated on the carbon susceptor by surface irradiation with a Xe lamp. Below the substrate temperature of 600°C, the growth rate of epitaxial Si films on (100) substrates is similar to that of polycrystalline Si films on the SiO₂/Si substrates, but it increases rapidly compared with that of polycrystalline Si, with an increase of the substrate temperature. This suggests that preferential growth appears for substrate temperature.



Fig. 3. Flow rate dependence of epitaxial growth rate on Si(100) substrates for Xe lamp irradiation.

peratures higher than 600°C. This suggestion is also supported by the result that the growth rate of epitaxial Si films on (100) substrates is higher than that on (111) substrates, as seen from Fig. 5.

Electron diffraction patterns of homoepitaxial films on Si (100) substrates revealed that the homoepitaxial Si films have been successfully grown at substrate temperatures of 550°C or higher (see Fig. 6). Figure 7(a) shows the surface morphology of the epitaxial Si film grown at the substrate temperature of 700°C after Wright etch treatment. No etch pits can be seen from this photograph. For further investigation of the epitaxial Si film quality, we have observed the oxidation-induced stacking fault (OSF) [see Fig. 7(b)]. Only small line defects have been observed. From these observations, it has been indicated that the epitaxial Si layer of high crystallographic perfection has been obtained at the substrate temperature of 700°C.

The level of impurities incorporated in the film during growth is extremely low, because of the high-rate growth in the clean environment. However, further investigation of the film formation process with *in situ* cleaning is necessary to obtain structurally perfect epitaxial silicon.

The base pressure in the reaction chamber is influenced by the heating method. The epitaxial growth of Si is very sensitive to the base pressure before the film formation. The influence of the base pressure in the chamber on the film quality can be seen from Fig. 8. The surface morphology of the epitaxial Si film grown at the base pressure of less than 5×10^{-8} torr for the Xe lamp heating is smooth compared with that at the base pressure of 1×10^{-6} torr for the IR lamp heating. The Si film grown on the Si substrate at 1×10^{-6} torr is polycrystalline and its morphology is similar to that of the Si film grown on the SiO₂/Si substrate. This is probably because the substrate surface has been



Fig. 4. Flow rate dependence of polycrystalline Si growth rate on SiO_2/Si substrates for Xe lamp irradiation.

oxidized under the base pressure of 1×10^{-6} torr where the moisture was mainly included and the very thin oxide layer has been formed on its surface.

The effect of the wavelength of the light on the growth rate at the substrate temperature of 700°C is shown in Fig. 9. The growth rate on Si substrates under the Xe lamp surface irradiation is higher than that under the IR lamps' surface irradiation, while the growth rate on SiO₂/Si substrates is not dependent on the wavelength of the lights. The difference in the growth rate on the Si substrates is considered to be caused by the excitation of electron-holes in the Si substrate by the xenon lamp. It is deduced that excited electron-hole pairs can induce the substrate temperature increase, mainly due to the surface recombination of electrons and holes, because of shallow penetration depth of about 10 µm in the Xe lamp irradiation (9) and enhancement of the surface chemical reaction by the creation of the electron-hole pairs. By using xenon lamp irradiation, the bare Si surface is selectively heated, compared with the SiO₂ surface, due to the thermal energy generated from the surface recombination process of the electronhole pairs. The recombination center is concentrated on the bare Si surface, where the diffused electron-hole pairs are recombined. On the other hand there exists little recombination center, due to dangling bonds, at the Si-SiO₂ interface.

The xenon lamp has wavelengths ranging from 300 nm to 1.1 μ m, having a peak wavelength of 0.8 μ m. About 70% of the Xe lamp irradiation energy is transferred to surface heating energy in the surface recombination process. Furthermore, the excited electron-hole pairs are concentrated in the depth of 10 μ m from the Si substrate surface, so that most electron-hole pairs are diffused to the surface recom-



Fig. 5. Flow rate dependence of epitaxial growth rate on Si(100) and (111) substrates for Xe lamp irradiation.

bination center, and the bare Si surface is selectively heated up due to a very low level of bulk recombination. In contrast, the IR lamp has wavelengths ranging from 300 nm to 5 μ m. In the case of the irradiation of a spreading wavelength light, whole Si substrates are heated up, because the electron-hole pairs are generated and spread over the depth of the Si substrate, and are also recombined at the lapped back face of the Si substrate.

Uniformity of the grown film thickness has been achieved, to about $\pm 2.5\%$ within a substrate (50 mm in diameter), in the case of the uniform substrate heating, because the growth rate was strongly controlled by the substrate temperature rather than the distribution of the source gas flux reaching the substrate surface. The film formation was concentrated on the substrate surface and on the heating susceptor surface. This means that this system presents a cleaning-free function with which the equipment does not need the manual cleaning procedure of the chamber. This result supports the interpretation that the film formation mechanism is dominated only by the surface reaction, because no clusters formed by the



Fig. 6. Reflective electron diffraction patterns of epitaxial Si layers grown at substrate temperatures of 550°, 600°, and 700°C.



Fig. 7. Surface morphology of (a) Wright etched film observed by scanning electron microscope and of (b) OSF observed by Nomarsky interference optical microscope.



Fig. 8. Surface morphology of the films grown under the base pressure of (a) 5 \times 10⁻⁸ torr for Xe lamp heating and (b) 1 \times 10⁻⁶ torr for IR lamp heating before film formation.

vapor phase reaction have been found on the chamber surface.

A model explaining these results is proposed as follows. Source gas molecules introduced through the gas nozzle directly reach the substrate surface (on which no stagnant layer is formed) by suppressing thermal convection without the vapor phase reaction, because the velocity of the source gas molecules is high. The source gas molecules adsorbed on the heating substrate surface are thermally decomposed only on the substrate surface. The surface reaction proceeds quickly, because the reaction by-product (H_2) is immediately removed from the substrate surface to the high vacuum environment. Consequently, high-rate surface reaction gives rise to the high-rate growth of the film.

Conclusions

In conclusion, it has been demonstrated that high-rate growth of epitaxial Si and polycrystalline Si films has been achieved by using free-jet molecular flow expanding into high vacuums. For the Si epitaxial growth, it has been found that the electron excitation in the adsorbed Si₂H₆ molecules, and the electron-hole excitation in the substrate with a xenon lamp, contribute to the high-rate growth. The homoepitaxial Si films have been successfully grown at substrate temperatures of 550°C or higher. It has been demonstrated that the newly developed system is cleaning-free because there is no deposition of reaction byproducts on the chamber inner surface. We believe that the film formation mechanism is dominated by the surface reaction, due to the complete suppression of the vapor phase reaction.

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Fig. 9. Effect of the wavelength of the light on the growth rate at the substrate temperature of 700°C.

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REFERENCES

- 1. F. C. Everstern, P. J. W. Severin, C. H. J. v. d. Brenkel, and H. L. Peek, *This Journal*, **117**, 925 (1970). 2. T. Ohmi, in "Proceedings of SEMI Technology Sympo-
- sium '86," Tokyo.
- 3. T. Ohmi, H. Kumagai, M. Morita, M. Itoh, T. Kochi, and M. Kosugi, Appl. Phys. Lett., 52, 1173 (1988).
- 4. T. Ohmi, H. Kumagai, M. Morita, M. Itoh, T. Kochi, M. Kosugi, and G. Tei, in "Advanced Materials for ULSI," Vol. 88-19, Y. Akasaka, M. Scott, and R. Reif, Editors, p. 36, The Electrochemical Society Softbound Pro-
- ceedings Series, Pennington, NJ (1988).
 5. T. Ohmi, N. Mikoshiba, and K. Tsubouchi, in "ULSI Science and Technology/1987," Vol. 87-11, S. Broydo and C. M. Osburn, Editors, p. 761, The Electrochemical Society Softbound Proceedings Series, Pennington, NJ (1997). NJ (1987)
- T. Ohmi, J. Murota, Y. Kanno, Y. Mitsui, K. Sugiyama, K. Kawasaki, and H. Kawano, in *ibid.*, p. 805.
- 7. T. Ohmi, M. Morita, E. Hasegawa, M. Kawakami, and K. Suma, Paper 160 presented at The Electrochemical Society Meeting, Los Angeles, CA, May 7-12, 1989. 8. M. Morita, T. Ohmi, E. Hasegawa, M. Kawakami, and K.
- Suma, 1989 Symposium on VLSI Technology, Kyoto,
- 9. S. Imai, Y. Ishihara, G. S. Jong, and T. Ohmi, in "Proceedings of the 7th ULSI Ultra Clean Technology Symposium," p. 242, Tokyo (1988).