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# High-rate growth at low temperatures by free-jet molecular flow: Surface-reaction film-formation technology

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Surface-reaction film-formation technology of epitaxial Si and polycrystalline silicon using free-jet molecular flow is proposed. High-rate ( $\sim 0.5 \mu\text{m}/\text{min}$  or higher) growth of homoepitaxial Si films with high crystallographic perfection has been achieved at temperatures as low as  $600^\circ\text{C}$  without the chemical by-product deposition on the inner surface of the reaction chamber. This result also implies that this system has the cleaning-free function. The film-formation mechanism appears to be dominated by the chemical reaction on the substrate surface without the vapor phase reaction.

In the chemical vapor deposition (CVD) method, which is extensively employed for the formation of various thin films, particularly in the very large scale integration (VLSI) process technologies, the source gases flow at a viscous flow, where a stagnant layer is inevitably formed on the substrate surface because of the thermal convection above the heating substrate susceptor.<sup>1</sup> Thus the source gas molecules are supplied onto the substrate surface by density diffusion through the stagnant layer. The viscous-flow gas supplying system essentially accompanies vapor phase reactions of source gas molecules, resulting in the creation of micro-particles that degrade the film quality and the deposition of a large amount of the chemical by-products on the inner surface of the chamber wall and the exhaust system. The excess molecules are wasted, increasing the energy spent on the fume scrubbing in the exhaust system. The by-products deposited on the chamber surface act as contamination sources in the film formation process while fabricating VLSI devices. The ceaseless 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 the decrease of the running time of the fabricating machine and the degradation of the environment cleanliness in the chamber, because the chamber wall is contaminated by air, particularly moisture, whenever the cleaning procedure is performed. Thus the conventional CVD includes the serious disadvantages described above. In this letter we describe a novel film-formation technology using free-jet molecular flow that is characterized by a film formation through surface reactions without accompanying vapor phase reactions, resulting in the cleaning-free function to keep the cleanliness in the reaction chamber during and after the film formation.<sup>2</sup>

It is very essential for the formation of high-quality films to satisfy the following conditions. (1) All source gases are directly introduced only onto the substrate surface to contribute the film growth. (2) The film formation is carried out through the surface reaction without the vapor phase reaction. (3) The chemical by-products are immediately eliminated from the substrate surface. As a way to satisfy these conditions, we propose to control the molecular flow pro-

duced by free jets expanding through the nozzle into high vacuums. The nozzle produces the high-velocity and low-temperature molecules expanding only for the substrate surface. The high-vacuum system enables the fast elimination of the chemical by-products from the substrate surface in addition to the high-velocity and low-temperature molecular flow.

The schematic diagram of the film-formation system that we have designed and set up is illustrated in Fig. 1. The inner surface of the stainless chamber is coated with a corrosion-resistant layer of TiN. The reaction chamber is always pumped down with a turbomolecular pump (2000  $\ell/\text{s}$ ) to pressures of less than  $5 \times 10^{-8}$  Torr. The silicon substrate is set flat on susceptor by the load-lock system with the electrostatic wafer chuck. The substrate is preferentially heated by the cathode voltage drop of glow discharge under the susceptor and by the irradiation of halogen lamps. The substrate temperature is monitored by a thermocouple buried in the pedestal. An ultraclean source gas ( $\text{Si}_2\text{H}_6$ ) is supplied into the chamber through the ultraclean gas delivering system.<sup>3</sup> The source gas ( $\text{Si}_2\text{H}_6$ ) is introduced through the gas nozzle ( $10 \mu\text{m}$  in diameter), forming the jet streams onto the substrate surface.

The substrates were B-doped (100) Si wafers with a diameter of 50 mm. Prior to the film formation, the Si substrates were chemically cleaned and etched, and the  $\text{SiO}_2$  ( $\sim 100 \text{ nm}$ )/Si substrates were produced by the thermal oxidation of Si substrates. To determine the film thickness,

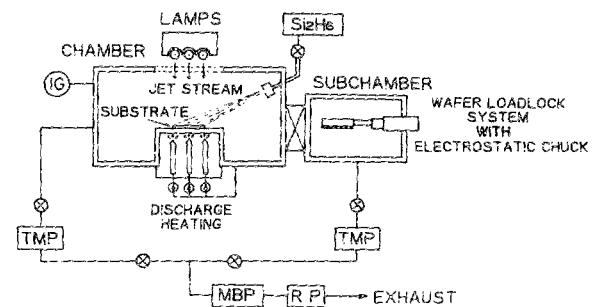


FIG. 1. Film-formation system.

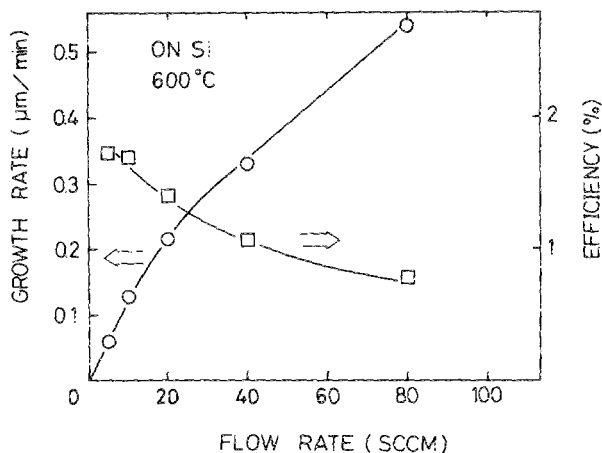


FIG. 2. Flow rate dependence of epitaxial growth rate and growth efficiency, which is defined as the ratio of the number of Si atoms in the growth film to that in the source gas supplied during the growth.

the Si substrates, on which SiO<sub>2</sub> layers were patterned like a stripe, were also used. The thicknesses of the films formed on the stripe substrates were determined by etching any area of the polycrystalline Si/SiO<sub>2</sub> layers and by using the surface profiler. The film formation was carried out at temperatures between 400 and 600 °C. The flow rates of Si<sub>2</sub>H<sub>6</sub> gas were varied from 5 to 100 sccm. The pressure near the chamber inner surface was approximately 10<sup>-3</sup> Torr during the film formation. The crystallographic structure was evaluated by high-energy electron diffraction and x-ray diffraction.

Figure 2 shows the flow rate dependence of epitaxial growth rate and growth efficiency, which is defined as the ratio of the number of Si atoms in the grown film to that in the source gas supplied during the growth. High-rate growth (~0.5 μm/min or higher) has been obtained at 600 °C for 80 sccm. This results in a high-speed flow of narrow expansion onto the substrate surface and the fast elimination of by-products from the substrate surface. Electron diffraction patterns of homoepitaxial films on *p*-Si (100) substrates revealed that the homoepitaxial Si films of high crystallographic perfection have been successfully grown at temperatures as low as 600 °C. It is inferred that the impurity level incorporated in the film during the growth is extremely low because of the high-rate growth in the clean environment. Thus a low-temperature Si epitaxial growth with a high rate has been achieved in our system. The film-formation rate of polycrystalline Si films, which is defined as the ratio of the film thickness to the formation time, is as high as that of epitaxial Si films at 450 °C and tends to decrease as the temperature elevates. It is likely that the preferential growth appears with the temperature increase.

The temperature dependence of epitaxial growth rate for 20 sccm is shown in Fig. 3, where the activation energy of the growth rate is 1.3 eV. Figures 2 and 3 indicate that the growth rate depends on both temperature and flow rate. This result implies that the epitaxial growth mechanism cannot be explained by the stagnant layer model.<sup>1</sup> This is considered to be mainly caused by the free-molecular-flow gas supply-

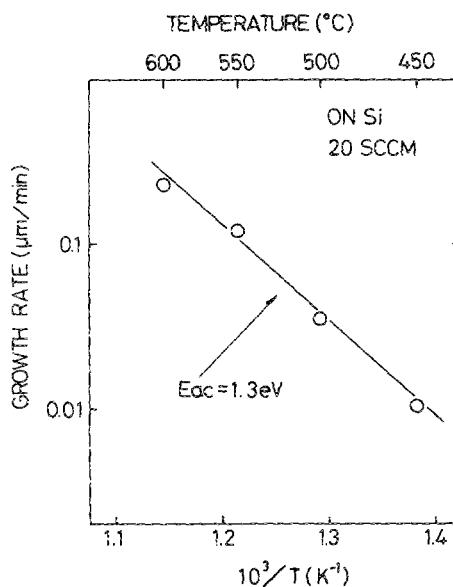


FIG. 3. Temperature dependence of epitaxial growth rate.

ing system to realize the slip flow of the gas molecules on substrate surfaces, because the gas pressure was maintained at the order of 10<sup>-3</sup> Torr during the growth. It is indicated in Fig. 2 that the growth efficiency decreases and the growth rate slightly saturates as the flow rate increases. This is interpreted to be caused by the cooling effect of the gas flow on the substrate surface.

The uniformity of the film thickness is achieved to about ± 2.5% within a substrate (50 mm in diameter) in the case of the uniform substrate heating, because the growth rate is 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 also supports the explanation that the film-formation mechanism is dominated only by the surface reaction, because no clusters formed by the vapor phase reaction could be found on the chamber surface.

A model explaining these results is proposed as follows: Source gas molecules (Si<sub>2</sub>H<sub>6</sub>) introduced through the gas nozzle directly reach the substrate surface (on which no stagnant layer is formed), overcoming the free convection without the vapor phase reaction, because the velocity and temperature of the source molecules are high and low, respectively. The molecules adsorbed on the substrate surface heated are thermally decomposed only on the substrate surface. The surface reaction proceeds fast, because the reaction by-product (H<sub>2</sub>) is immediately eliminated from the substrate surface to the high-vacuum environment. Consequently high-rate surface reaction gives rise to the high-rate growth of the film.

In conclusion, we have demonstrated that high-rate growth of epitaxial Si and polycrystalline Si films is achieved by using molecular flow formed by free jets expanding into high vacuums. The homoepitaxial Si films of high crystallo-

graphic perfection have been successfully grown at temperatures as low as 600 °C. It has been found that our system has the cleaning-free function. We believe that the film-formation mechanism is dominated by the surface reaction to realize high-quality films.

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