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Doping Technology for Silicon Thin Films Grown by Temperature-Modulation Molecular Layer Epitaxy

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Layer-by-layer growth of single-crystalline Si with doping was achieved by a temperature-modulation (TM) method combined with an intermittent supply of Si_2H_6 and dopant precursor B_2H_6 for p-type growth on Si(100). B_2H_6 was introduced at a predetermined timing of supply in several doping modes. This TM Si molecular layer epitaxy enabled the growth of a flat surface with layer-by-layer growth in a self-limiting manner on Si(100) and with an outstanding high carrier concentration of over 5×10^{20} cm^{-3} while maintaining selective epitaxy at the maximum temperature of 470°C. Based on the results of doping in several modes of growth, the incorporation mechanism of dopant on the growing surface is discussed with respect to the TM process.
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Recent progress in silicon devices has increased the importance of small-scale fabrication techniques. Technological advances in the growth of high-quality silicon layers with atomically accurate thickness control are required before such high-speed devices with nanometer-scale structures can be fabricated. Low-temperature and low-damage processing techniques are suitable for the fabrication of nanostructures, because the amounts of change of the doping profile and defect density can be decreased. To achieve this, Nishizawa *et al.* developed the atomic layer epitaxy (ALE) technique for the growth of single-crystalline Si[1] and referred to the method as molecular layer epitaxy (MLE).[2] In Si MLE, growth is performed by alternating the supply of SiH_2Cl_2 and H_2 at the optimal temperature of 825°C.[1] Lowering the growth temperature to 540-650°C was achieved by alternately supplying SiH_2Cl_2 and atomic hydrogen.[3] However, this temperature is still too high for the fabrication of fine structures with doping profiles of sub-0.1 μm order. In the case of Si nanostructure device fabrication processes, high-quality doped layers are desired for the fabrication of heavily doped abrupt structures. Hence, a low-temperature growth technique with atomic- and molecular-level controllability using the well-known hydrides SiH_4, Si_2H_6, and Si_3H_8 is considered essential.[4-6] Recently, we have reported the growth method called temperature-modulation (TM) Si MLE using Si_2H_6[7-9] in which the growth thickness per cycle saturated at 0.3 monolayers when Si_2H_6 supply was sufficient. According to an *in situ* observation of the Si surface reaction by real-time mass spectroscopy,[7] Si submonolayer growth is dominated by the self-limiting adsorption of Si-H compounds at 380-480°C and the desorption of hydrogen at 530°C.[9] However, surface roughness due to three-dimensional growth was considerable at the modulation temperature of 530°C. Surface morphology was improved drastically by inducing two-dimensional growth by lowering the modulation temperature to 470°C.[8]

In this work, TM Si MLE growth with doping has been studied using the intermittent supply of Si_2H_6 and a dopant precursor, B_2H_6, for p-type growth on Si(100).

Experimental

Figure 1 shows the growth sequence of TM Si MLE without doping and the experimental setup used in this study for growth with doping. The system consists of a growth chamber, gas supply control system for Si_2H_6, B_2H_6, and PH_3, a heating lamp system, a temperature-control system with an optical pyrometer, a load-lock chamber, and a vacuum pump system. The base pressure of the growth chamber is about 1×10^{-8} Pa. The substrates were heated using a heating lamp, and the temperature was monitored and controlled using the pyrometer, the output signal of which was coupled to the control unit of the heating lamp system. The pyrometer was calibrated by the temperature measured directly using a Pt-Pt·Rh (13%) thermocouple. Si(100) phosphorus-doped n-type wafers fabricated by the Czochralski method (approximately 10 Ω cm) were used as substrates. In order to determine the Si epitaxial layer thickness, the wafers were partially masked with SiO_2 by thermal oxidation and photolithography. After surface treatment by $H_2SO_4:H_2O_2$, $HCl:H_2O_2:H_2O$, and diluted HF, the substrate was placed into a load-lock chamber and transferred into the growth chamber. The etched depth of the Si surface as a result of the diluted HF treatment

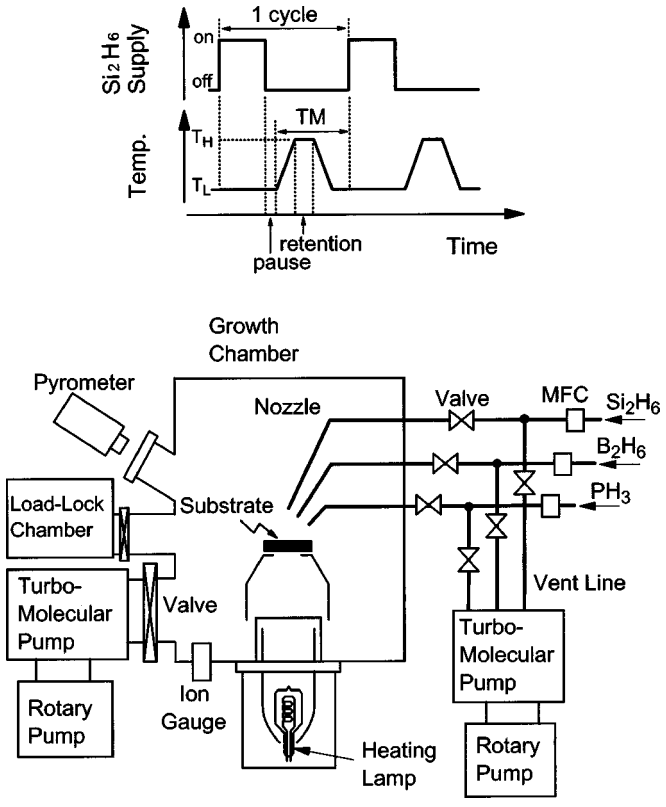

Figure 1. Schematic illustration of a growth sequence and TM Si MLE system with doping.

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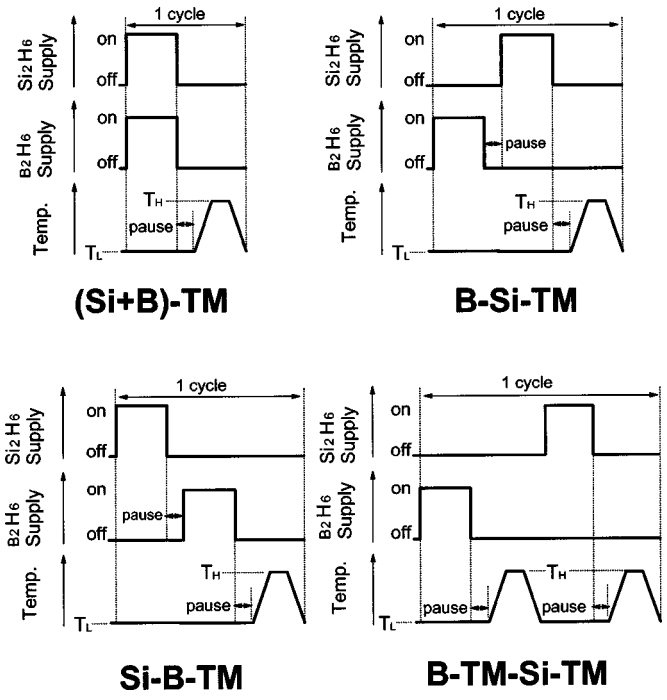

Figure 2. Growth modes for boron-doped films. (Si + B)-TM: Si_2H_6 and B_2H_6 are supplied at the same time intermittently followed by TM. B-Si-TM: intermittent B_2H_6 supply is followed by intermittent Si_2H_6 supply and TM. Si-B-TM: intermittent Si_2H_6 supply is followed by intermittent B_2H_6 supply and TM. B-TM-Si-TM: intermittent B_2H_6 supply is followed by TM, which in turn is followed by intermittent Si_2H_6 supply with subsequent TM.

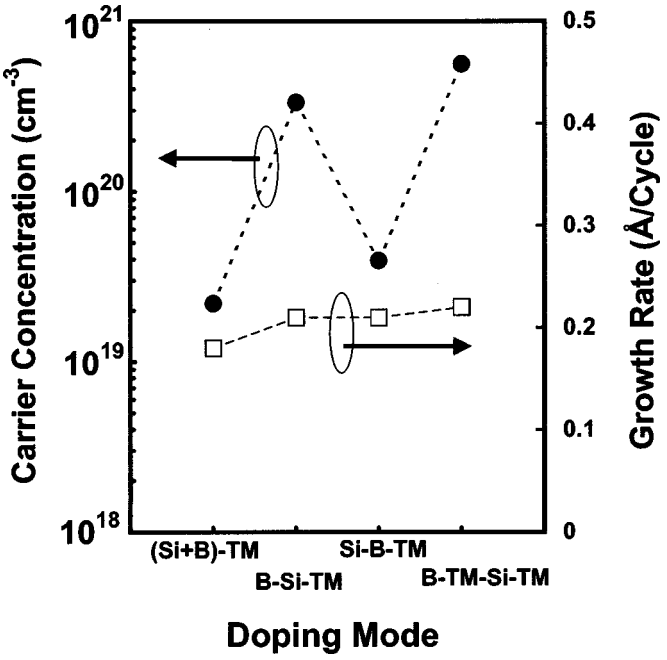

Figure 3. Carrier concentration and growth rate per cycle of boron-doped film grown in each mode. The supply duration of Si_2H_6 and B_2H_6 was 4 s at 1.8 and 0.5 sccm flow, respectively, and the pauses were constant at 1 s in all modes. In the TM process, heating time from T_L (400°C) to T_H (470°C) was 6 s, and cooling time was 5 s.

was 1 nm, by which the thickness of the epitaxial layer was calibrated. Prior to epitaxial growth, the substrate was heated in the growth chamber to a temperature of approximately 600°C for 30 s to remove adsorbed impurities. Undoped growth by Si MLE was performed cyclically, as shown in Fig. 1. The Si_2H_6 (99.99%) source was introduced under a controlled flow rate for a constant duration at temperature T_L, then the TM process was performed. In the TM process, the substrate temperature was raised from T_L to the modulated temperature, T_H, and then cooled to T_L again. This periodic gas supply and TM process were repeated until the desired layer thickness was obtained. To obtain an atomically flat surface morphology and to achieve selective epitaxy, T_H was fixed at 470°C. The epitaxial layer was selectively grown on the Si surface and no growth or deposition occurred on the patterned SiO_2 mask at T_H of 470°C. To determine the growth thickness, the steps formed by epitaxial growth were measured using a microstylus profilometer after the removal of SiO_2.

In this study, B_2H_6 (5% B_2H_6 in N_2) was used as the dopant precursor for p-type epitaxial growth. The dopant precursor was also introduced intermittently on the surface in the TM process. This periodic gas injection process was repeated until the desired film thickness was obtained. The p-type layers doped with boron were grown on n-type wafers, and the carrier concentrations of the grown layers were set significantly higher than that of the wafers. Accordingly, the carrier concentration of the grown films was measured by the van der Pauw method at room temperature without any correction.

Results and Discussion

Thin, undoped Si epitaxial layers were fabricated by the TM Si MLE method using Si_2H_6 gas at T_L of 400°C and T_H of 470°C. With the decrease of T_H from 530 to 470°C, the surface morphology was improved drastically from a three-dimensional island feature to a two-dimensional atomically flat surface. The growth rate per cycle decreased with decreasing T_H, and 0.2 Å/cycle at 470°C, which means 15% of the monolayer value for Si. On the basis of undoped film growth, boron-doped p-type Si growth was examined with four modes of gas supply and TM, as shown in Fig. 2. In the first mode, as indicated by mode (Si + B)-TM, Si_2H_6 and B_2H_6 are supplied at the same time intermittently at T_L, and then the TM process is performed after stopping the supply of gases. In the second mode, B_2H_6 is supplied intermittently followed by an intermittent Si_2H_6 supply at T_L, and the TM process is performed: mode B-Si-TM. As

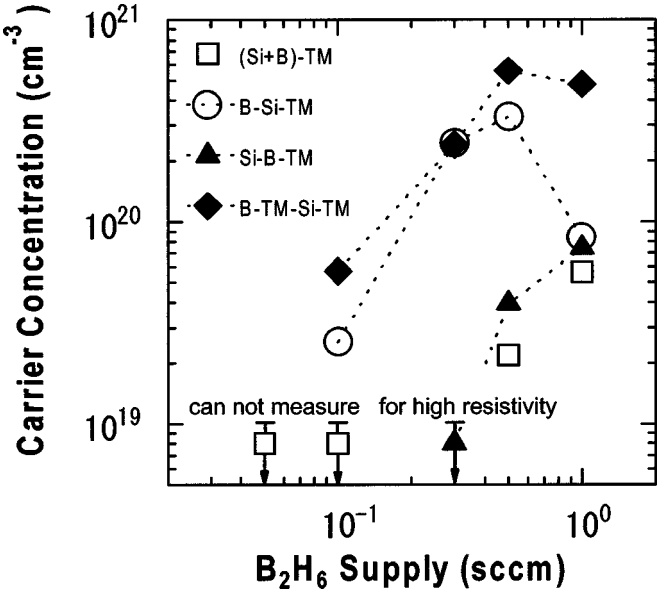

Figure 4. Dependences of the growth rate and the carrier concentration of boron-doped p-type layer on B_2H_6 supply in each mode.

the third mode, Si-B-TM, an intermittent supply of Si_2H_6 followed by B_2H_6 and the TM process is also examined. Finally, in mode B-TM-Si-TM, B_2H_6 is supplied intermittently followed by TM, and Si_2H_6 is supplied intermittently followed by TM. These modes were repeated for 600 cycles, and the characteristics of the grown layer were measured.

The duration of Si_2H_6 and B_2H_6 supply was 4 s, and the pauses were constant at 1 s in all modes. In the TM process, the heating time from T_L to T_H was 6 s at the rate of 11.6°/s, and the cooling time was 5 s at 14.0°/s with 0 s of retention.

Figure 3 shows the carrier concentration and the growth rate per cycle of boron-doped film grown by each mode. In each mode, the volumes of Si_2H_6 and B_2H_6 (5% B_2H_6 in N_2) supply are constant at 1.8 and 0.5 sccm, respectively. In spite of the same amount of B_2H_6 supply in one cycle of each mode, the difference among modes was considerable. The highest carrier concentration in the grown film was obtained in the B-TM-Si-TM mode, followed by the B-Si-TM mode, whereas the films grown in the (Si + B)-TM and Si-B-TM modes showed about one order lower carrier concentration. Since the growth rates were not greatly influenced in each mode, the Si-H adsorption process might not be influenced by the coverage of boron compound. However, the coverage of boron compounds formed after B_2H_6 supply is influenced by the mode. The grown surface was atomically flat, and the epitaxial layer was selectively grown on the Si surface; no deposition occurred on the patterned SiO_2 mask. This tendency was observed independently of the mode of growth. In addition, single-crystalline film growth on the Si(100) surface was confirmed by reflection high-energy electron diffraction (RHEED) measurement.

The dependences of the carrier concentration of a boron-doped p-type layer on B_2H_6 supply in each mode are shown in Fig. 4. The carrier concentration in each mode increased with increasing B_2H_6 supply in the range up to 0.5 sccm. A high carrier concentration was achieved by growth in modes B-Si-TM and B-TM-Si-TM, in this range of B_2H_6 supply. This result means higher doping efficiency may be realized by supplying B_2H_6 to the growing surface just after the TM process. The surface after the TM is assumed to be fresh, because the adsorption species of the materials and by-products, for example, can release from the surface by higher temperature TM process. Therefore, boron compound incorporation from B_2H_6 on the surface after TM can be increased in modes B-Si-TM and B-TM-Si-TM. In addition, in these modes, supply of excess B_2H_6, as occurs at 1 sccm, leads to the decrease of carrier concentration. This means that the amount of nonactive boron electrically increases with increasing amount of B_2H_6 under excess supply.

On the other hand, over one order of magnitude lower carrier concentration was obtained in modes (B + Si)-TM and Si-B-TM than in modes B-Si-TM and B-TM-Si-TM. This indicates that an interactive competitive adsorption occurs between a boron compound and a silicon compound in mode (B + Si)-TM, because B_2H_6 and Si_2H_6 are introduced at the same time on a fresh surface that is formed by the TM process on Si(100). The competitive adsorption reduces the doping efficiency by over one order of magnitude compared with the growth in a high-efficiency mode. This competitive adsorption phenomenon should be dominant for conventional growth processes, for example, vapor phase epitaxy and molecular beam epitaxy (MBE) using gas sources. In other words, TM Si MLE with doping enables the control of the elemental process steps of impurity incorporation and is advantageous for achieving effective doping in the Si process.

Figure 5 shows the relationship between Hall mobility and the carrier concentration of boron-doped p-type film for each mode of doping. The mobility of the films grown in modes B-Si-TM and B-TM-Si-TM showed higher values than those of the films grown in other modes. In particular, the characteristics of the film grown in mode B-TM-Si-TM showed the highest mobility, in addition to the maximum doping efficiency, as shown in Fig. 4. In the region of heavy doping of above 5×10^{20} cm^{-3} of carrier concentration in mode B-TM-Si-TM with 1 sccm B_2H_6 supply, the segregation of boron is assumed to occur because the Hall mobility decreases as the B_2H_6 supply increases. Details of the behavior of segregated boron will be discussed in another paper.

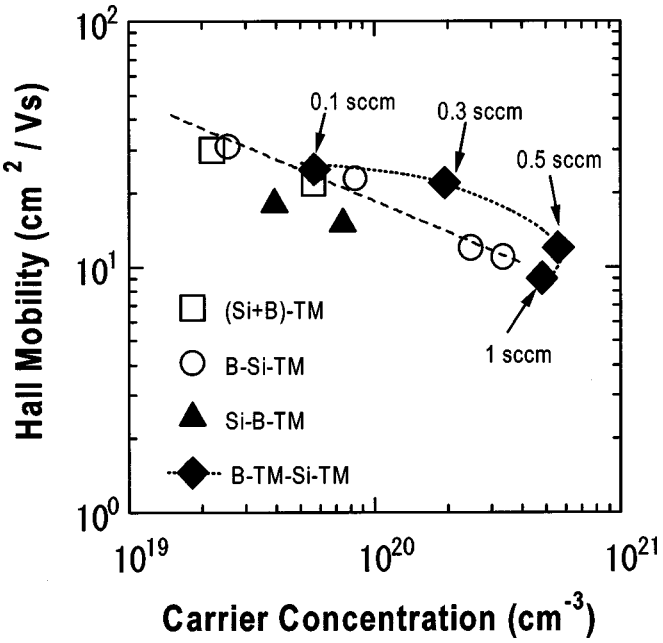

Figure 5. Relationship between Hall mobility and the carrier concentration of boron-doped p-type film for each doping mode.

Conclusions

We achieved TM Si MLE growth with doping by intermittently supplying Si_2H_6 and dopant precursor B_2H_6 to induce p-type growth on Si(100). TM Si MLE under the conditions of an intermittent Si_2H_6 supply at 400°C followed by the TM process at 470°C enabled the growth of an atomically flat surface with layer-by-layer growth in a self-limiting manner on Si(100). B_2H_6 was introduced at a predetermined timing of supply in several doping modes in TM Si MLE. The higher carrier concentration was achieved by supplying B_2H_6 to the growing surface just after the TM process, in growth modes B-Si-TM and B-TM-Si-TM. The carrier concentration of over 5×10^{20} cm^{-3} was attained while maintaining selective epitaxy.

The surface after the TM process is assumed to be fresh based on the desorption at higher temperature, therefore, the amount of boron compound incorporation into the surface after TM can be increased. On the other hand, competitive adsorption is dominant in conventional growth methods. The intermittent injection of Si_2H_6 and B_2H_6 followed by the TM process in our method will be advantageous in the future for achieving effective doping at low temperature.

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