

Nucleation Control of Silicon-Germanium on Silicon Oxide for Selective Epitaxy and Polysilicon Formation in Ultraclean Low-Pressure CVD

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Nucleation processes on Si oxide and epitaxial growth on Si for Si-Ge deposition have been investigated by ultraclean low-pressure CVD using SiH_4 and GeH_4 gases. It is found that, with GeH_4 addition, the deposition rate on Si increases and the nucleation rate decreases, and the degree of nucleation strongly depends on the Si oxide material. High selective Si-Ge epitaxy has been realized between Si and Si oxide at temperatures as low as 550°C . Moreover, it is suggested that control of the grain size of the deposited polysilicon film on Si oxide is possible by the Si-Ge nuclei.

INTRODUCTION

Low-temperature selective Si-Ge epitaxy is very important for the progress in future semiconductor devices, e.g. three-dimensional devices and heterodevices, because of the possibility of low-temperature selective Si-Ge epitaxy to tailor the band gap of heterostructure(1) and fill up via-holes. Because initial nucleation strongly influences grain size of polysilicon, and because the electrical properties of polysilicon depend on the grain size(2), the nucleation control on Si oxide is very important not only to perform selective epitaxy on Si, but also to fabricate high performance polysilicon for thin film transistors. However, very little is known about nucleation mechanisms. In previous works(3), it has been found that nucleation on Si oxide is suppressed, and low temperature selective Si epitaxial growth between Si and Si oxide has been realized as a result of ultraclean processing. In the present work, nucleation processes on Si oxide and

epitaxial growth on Si were investigated by ultraclean low-pressure CVD using SiH_4 and GeH_4 gases. The Si-Ge nucleus density on Si oxide was controlled at temperatures as low as 550°C , and Si-Ge fillings were realized in via-holes opened in Si oxide on Si(100) substrate. Furthermore, it is suggested that the grain size of the deposited polysilicon film on Si oxide is controlled by Si-Ge nuclei.

EXPERIMENTAL

The growth experiments were carried out

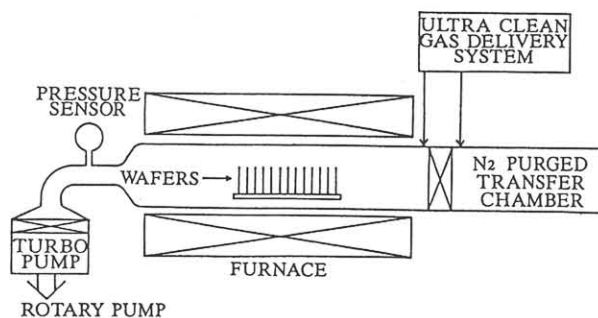


Fig.1. Schematic diagram of an ultraclean hot-wall low-pressure CVD system.

using an ultraclean hot-wall low-pressure CVD system shown in Fig.1(3,4). In order to investigate the nucleation processes on Si oxide and the epitaxial growth on Si, the samples were exposed to a $\text{SiH}_4\text{-GeH}_4\text{-H}_2$ gas mixture at 550°C . Subsequently, Si films were deposited using a $\text{Si}_2\text{H}_6\text{-H}_2$ gas mixture at 500°C . The influence of annealing in N_2 atmosphere on the structure has been investigated.

The substrates used were p-type Si wafers of 2-20 ohm-cm with mirror polished (100) and (111) surfaces. The nucleation was investigated on a thermal Si oxide, CVD-PSG(8wt.%), CVD-BSG (4wt.%), CVD-BPSG(B and P: each 4wt.%) and CVD- SiO_2 . To investigate the selectivity between Si and Si oxide, the Si oxide was locally removed. Before deposition, the wafers were cleaned several times in a 4:1 solution of H_2SO_4 and H_2O_2 , high-purity DI water and 1% HF.

The surface morphology and cross section of the samples were observed with a scanning electron microscope(SEM). The

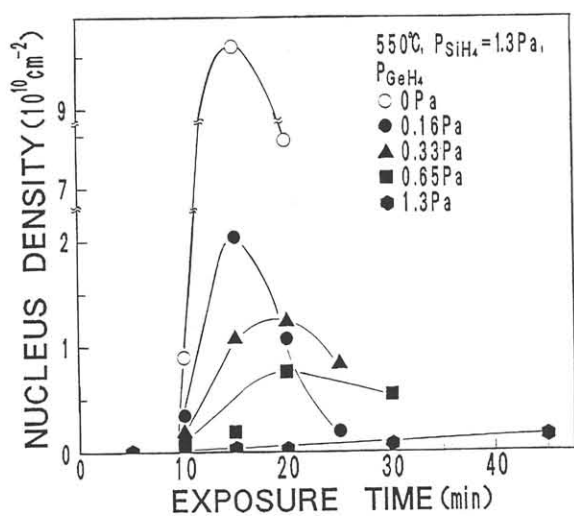


Fig.2. Dependence of the nucleus density on the exposure time of thermal SiO_2 to $\text{SiH}_4\text{-GeH}_4\text{-H}_2$ gas mixture for various GeH_4 partial pressures, P_{GeH_4} at a temperature of 550°C . The total pressure is 27 Pa and the SiH_4 partial pressure 1.3 Pa.

deposited thickness was measured by a Tencor Alpha Step. The structure of the films was evaluated by electron diffraction and x-ray diffractometry.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of the nucleus density on the exposure time of thermal SiO_2 to SiH_4 with various GeH_4 partial pressures. After the incubation period, the nucleus density increases up to a maximum value and then decreases with continued exposure time by the coalescence of nuclei. The nucleation rate decreases drastically with increasing GeH_4 partial pressure, although the incubation period is not influenced by the GeH_4 partial pressure. The maximum value of the nucleus density is determined by the balance of nucleation and coalescence(4). Figure 3 shows the surface morphology of various Si oxides exposed to $\text{SiH}_4\text{-GeH}_4\text{-H}_2$ gas mixture for 20 min at 550°C . It is found that the nucleus densities on PSG and BSG surfaces are lower than that on thermal SiO_2 . It is considered that the adsorption site densities on PSG and BSG surfaces are lower than that on thermal SiO_2 (4).

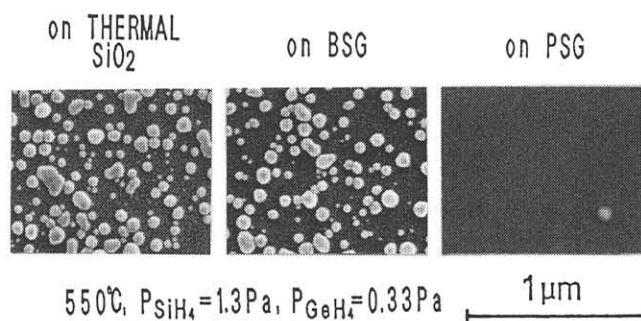


Fig.3. SEM micrographs of various Si oxide surfaces exposed to $\text{SiH}_4\text{-GeH}_4\text{-H}_2$ gas mixture for 20 min. The deposition conditions are the same as in Fig.2, except for the GeH_4 partial pressure.

Figure 4 shows the influence of GeH_4 addition on the deposition rate on Si substrate at 550°C . With GeH_4 addition, the deposition rate increases drastically, as reported(5), and the deposition rate on Si(100) becomes much larger than that on Si(111). Electron and x-ray diffraction measurements showed that epitaxial Si-Ge alloys were formed with GeH_4 addition.

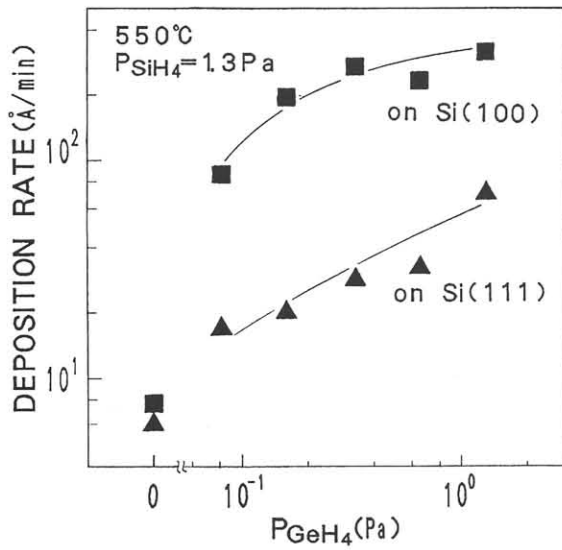


Fig.4. GeH_4 partial pressure dependence of the deposition rate on Si(100) and Si(111). The deposition conditions are the same as in Fig.2.

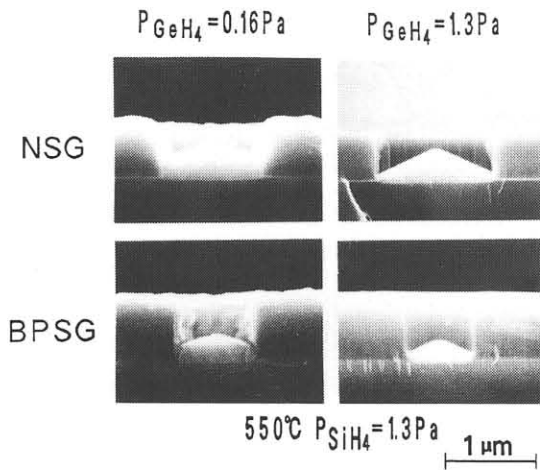


Fig.5. SEM micrographs of Si-Ge fillings formed in via-holes.

The Ge content estimated from the lattice constant was in good agreement with that evaluated by electron spectroscopy for chemical analysis(5). Therefore, it is believed that Ge atoms are uniformly incorporated into the films. Moreover, it was found that the Ge content in the film deposited on Si(111) is larger than that on Si(100).

As described above, it is clear that, with GeH_4 addition, the deposition rate on Si increases and the nucleation rate decreases, and the degree of nucleation strongly depends on the Si oxide material. This means that there are high selective growth conditions. It is found in Fig.5 that a perfect selective deposition is

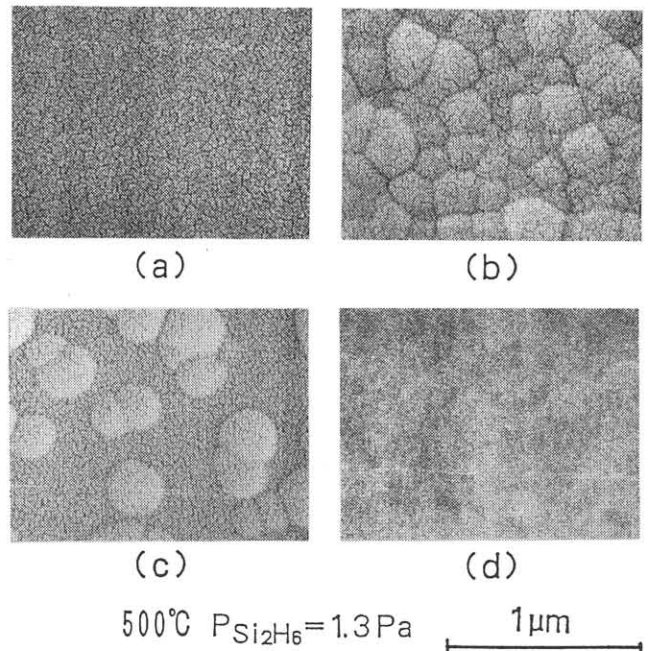


Fig.6. SEM micrographs of Si film surfaces deposited on thermal SiO_2 for 330 min at 500°C and a Si_2H_6 partial pressure of 1.3 Pa. Before the Si film formation, the SiO_2 surfaces were exposed to a SiH_4 - GeH_4 - H_2 gas mixture under a total pressure of 27 Pa at 550°C . GeH_4 partial pressure was (a) 0 Pa, (b) 0.65 Pa and (c) 1.3 Pa, and SiH_4 partial pressure 1.3 Pa, and the exposure time was 20min. Sample (d) has not been exposed.

obtained for CVD-BPSG, at low temperatures such as 550°C.

After Si-Ge nucleation control on thermal SiO₂, Si films were deposited subsequently in a Si₂H₆-H₂ gas mixture at 500°C. Typical SEM observation of the surfaces is shown in Fig.6. With an increase in GeH₄ partial pressure during the nucleation, the grain size increases and the number of grains decreases(Fig.6 (a)-(c)), while the sample surface without nucleation(Fig.6(d)) is flat, which means amorphous structure, as it will be described below. It is considered that vapor- and/or solid-phase epitaxial growth on nucleus surfaces occurs, while amorphous Si is formed on thermal SiO₂ during deposition at 500°C. The optimum conditions to cover the whole surface with grains are determined by the number of nuclei and the vapor- and/or solid-phase epitaxial growth rate.

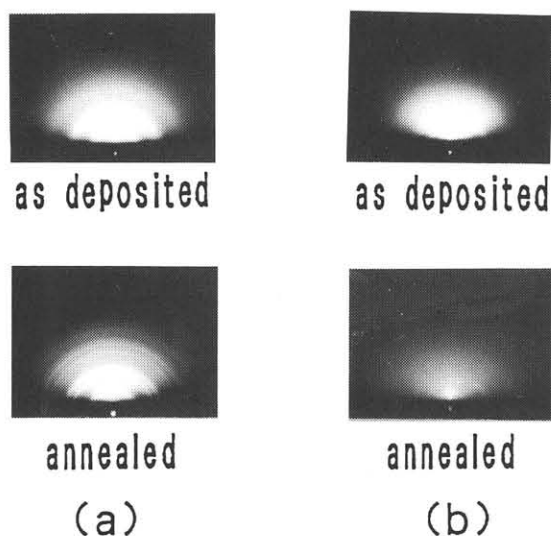


Fig.7. Typical electron diffraction patterns of Si film surfaces, as-deposited and annealed at 600 °C. Samples (a) were exposed under a total pressure of 27 Pa at 550°C, a SiH₄ partial pressure of 1.3 Pa and a GeH₄ partial pressure of 0.65 Pa. Samples (b) have not been exposed. The Si film deposition condition is the same as in Fig.6.

Figure 7 shows a comparison of electron diffraction patterns of sample surfaces as-deposited, with those annealed for 1 hour at 600°C. The samples without nucleation have an amorphous pattern for both, as-deposited and annealed. On the other hand, the as-deposited sample with nucleation has a random-oriented, polycrystalline pattern. Furthermore the pattern is changed by annealing to a stronger polycrystalline one. The crystallization of deposited Si films due to Si-Ge nuclei formed on thermal SiO₂ by using ultraclean CVD processing is very effective for the control of the grain size.

ACKNOWLEDGMENTS

The authors wish to express their gratitude for the encouragement of Prof. T.Ohmi in executing this study. CVD reactor was provided by Kokusai Electric Co. Ltd., and high-purity GeH₄ and Si₂H₆ were made available by Mitsui Toatsu Chemicals Inc. and Toagosei Chemical Industry Co., Ltd., respectively. The work was carried out in the Superclean Room of the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University.

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