Deposition of Epitaxial Silicon by Hot-Wall Chemical Vapor Deposition (CVD) Technique and its Thermodynamic Analysis

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Abstract

Epitaxial Si layers were deposited on n- or p-type Si (100) substrates by hot-wall chemical vapor deposition (CVD) technique using the SiH_2Cl_2-H_2 chemistry. Thermodynamic calculations of the Si-H-Cl system were carried out to predict the window of actual Si deposition process and to investigate the effects of process variables (i.e., the deposition temperature, the reactor pressure, and the source gas molar ratios) on the growth of epitaxial layers. The calculated optimum process conditions were applied to the actual growth runs, and the results were in good agreement with the calculation. The experimentally determined optimum process conditions were found to be the deposition temperature between 900 and 925℃, the reactor pressure between 2 and 5 Torr, and the source gas molar ratio (H_2/SiH_2Cl_2) between 30 and 70, achieving high-quality epitaxial layers.

1. Introduction

Demands for defect-free (1 ~ 10 defects/cm^2) substrates have been rapidly increased as the integrated circuits (IC's) based on Si become more complex1). Epitaxial deposition provides a means of forming single crystal layers with an impurity concentration independent of the substrate, and under certain conditions, epitaxial deposition can be made selectively with respect to a masking layer. Both of these epitaxial deposition characteristics can be used to make IC's more compact2,3).

The cold-wall CVD technique is frequently used in the industry to grow epitaxial Si layers on polished single crystal Si substrates, in which the substrates are only heated, while the reactor wall remain cold. The cold-wall CVD technique has merits on the quality of grown epi-layers and the reliability of process control, but the major drawback lies on the relatively low productivity. The hot-wall LPCVD technique, on the other hand, can typically provide higher productivity, and thus this technique is mostly used to deposit polycrystal Si layers in a large batch (~100 wafers/batch)1).

This study reports the epitaxial growth of Si on polished Si (100) substrates using hot-wall LPCVD technique. The main objective was to find the optimum epitaxial growth conditions of the hot-wall process for the application in the commercial reactor development. High-throughput, multi-wafer LPCVD reactor system was thus employed for this study, and the SiH_2Cl_2-H_2 chemistry was adopted. Thermodynamic calculations of the deposition process were first carried out to predict the process windows, and these calculated conditions were applied to the actual growth runs. The effects of various process variables on the growth of epitaxial Si layers were then experimentally investigated, and the properties of grown epi-layers were analyzed.

2. Thermodynamic simulation

A complex thermodynamic simulation of the hot-wall CVD process was performed through calculation of equilibrium compositions of reactants and products. The simulation involved the equilibrium calculations of multi-phase, multi-component mixture with chemical reactions. The thermochemical system of this study involved 3 components (Si-H-Cl) and 3 phases (gas, liquid, and solid phase).

First, all the important chemical species in the system were thoroughly investigated, and their thermochemical data were carefully selected and reviewed from the literature[4-11)]. The selected chemical species were total 22 vapor phase species and 2 condensed phase species (liquid Si and solid Si).

Stoichiometric algorithm was adopted to carry out the calculations, and the effects of process variables (the deposition temperature, the reactor pressure, and the molar ratios of input gases) on the epitaxial growth were investigated, resulting the vapor phase mole fractions of all the selected chemical species at equilibrium, the equilibrium deposition yield, and the CVD phase diagrams of Si deposition.

3. Experimental

The growth system used in this study was a vertical hot-wall LPCVD system and consisted of 3 chambers (load-lock, loading, and growth chambers). The reactor body was made of quartz and heated by a vertical radiant heater. The source gases, SiH_2Cl_2 (dichlorosilane: DCS) and H_2 were introduced into the reactor through a specially designed quartz feeder, which minimized the pre-cracking of SiH_2Cl_2 gas by a jacketed N_2 coolant flow. Hydrogen was purified by a Pd-alloy H_2 purifier followed by a polymer resin type purifier, which effectively removed oxygen and water vapor to a level of < 10 ppb.

N- or p-type Si (100) substrates were cleaned by a typical RCA cleaning procedure and inserted into the quartz wafer cassette, which were then loaded into the reactor. The substrates were prebaked at 925℃ and 5 Torr for 30 min. before deposition. The substrates were rotated at 13 rpm during deposition to improve the deposition uniformity.

The surface quality of epitaxial layers was characterized by an optical microscope and SEM after SECCO etching. A spreading resistance profiler (SRP) was used to measure the epi-layer thickness and thickness uniformity.

4. Results and Discussion

Fig. 1 shows an example of calculated equilibrium vapor phase mole fractions of the Si-H-Cl system as a function of the deposition temperature. As clearly shown in the figure, the major vapor phase species in the reactor above 850℃ are H_2, HCl, and $SiCl_2$. The mole fraction of $SiCl_2$ (major film precursor) increases with the growth temperature (T_g), until it reaches a nearly constant value above 1000℃ at a reactor pressure (P_T) of 5 Torr.

Fig. 2 shows the calculated mole yield of Si as a function of temperature at various reactor pressures. It can be seen in the figure that the deposition yield shows a maximum as temperature increases, but the yield is not a strong function of temperature between 800 and 1100℃ as long as the reactor pressure stays between 0.1 and 10 Torr.

A series of thermodynamic calculations revealed that the suitable operating process windows were the T_g between 850 and 1100℃, the P_T between 0.1 and 10 Torr, and the H_2/DCS ratio between 10 and 100.

These calculated optimum process conditions were then tested in the actual growth runs and fine-tuned based on the results of the grown epi-layer qualities. Fig. 3(a) and Fig. 3(b) show the typical SEM images of the grown epitaxial layers after SECCO etching. Excellent epitaxial layers could be repeatedly grown by the hot-wall LPCVD technique with optimum deposition conditions of the T_g between 900 and 925℃, the P_T between 2 and 5 Torr, and the H_2/DCS ratio between 30 and 70. Conventional etch-pit tests by an optical microscope could not reveal any surface defects, indicating the excellent quality of the epi-layers. The measured growth rate by SRP was about 0.035 μm/min., but it could be further increased by increasing the deposition temperature.

Thermodynamic simulation could predict the actual deposition process pretty well in this study, since the hot-wall LPCVD reactor configuration and the steady state gas flow condition involved in this study provided near-isothermal environment in the actual growth runs, and the relatively high temperature and the low pressure provided near-equilibrium conditions[12-14].

5. Acknowledgements

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6. References

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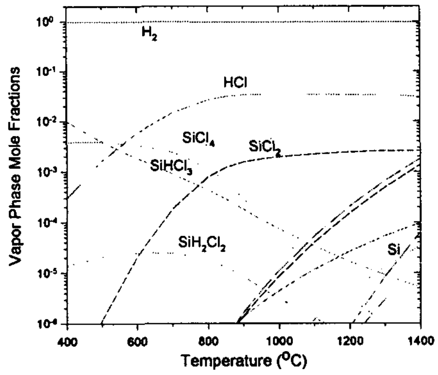


Fig. 1. Equilibrium vapor phase mole fraction of the Si-H-Cl system : P_T = 5 Torr; H_2/DCS = 50; X_{H_2} = 0.98

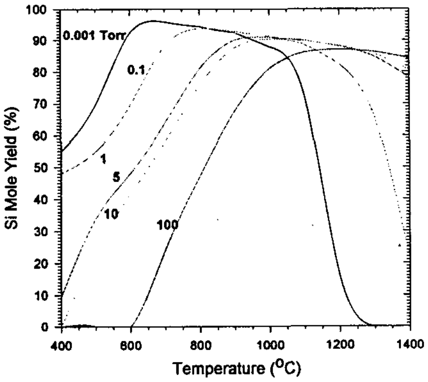
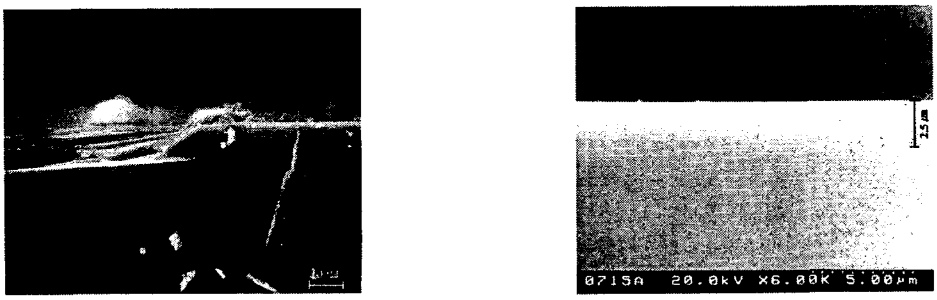


Fig. 2. Equilibrium mole yield of Si : H_2/DCS = 50; X_{H_2} = 0.98



(a) (b)

Fig. 3. Cross-sectional SEM images of Si epitaxial layers :
(a) T_g = 925℃; P_T = 1 Torr; H_2/DCS = 15
(b) T_g = 925℃; P_T = 2.7 Torr; H_2/DCS = 10