

Epitaxial Growth of Strained $\text{Si}_{1-x}\text{C}_x$ on Si and Its Device Applications

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Characterization of $\text{Si}_{1-x}\text{C}_x$ alloys on Si(001) grown by photo- and plasma-CVD are presented. We obtained the epitaxial $\text{Si}_{1-x}\text{C}_x$ films with C_2H_2 , CH_4 or $\text{SiH}_2(\text{CH}_3)_2$ addition to SiH_4 and H_2 gases at a substrate temperature of 200°C . Hydrogen incorporation in the epitaxial films was observed and these H atoms could be desorbed by thermal annealing. Local vibration mode (607cm^{-1}) of C in Si was detected in the films annealed at 700°C . X-ray reciprocal lattice space mapping indicated the pseudomorphic growth of $\text{Si}_{1-x}\text{C}_x$ alloys. The highest substitutional C content of 3.5 atomic% was obtained in the films with $\text{SiH}_2(\text{CH}_3)_2$ addition. *In-situ* phosphorus doping was also carried out by using PH_3 . The electron concentration of $\text{Si}_{1-x}\text{C}_x$ film was lower than that of Si film at the same PH_3/SiH_4 ratio. However, the value was increased up to the same level of the Si film after annealing at 700°C , which was $5 \times 10^{18} \text{cm}^{-3}$. It means that the dopant neutralization occurred in the as-grown $\text{Si}_{1-x}\text{C}_x$ films.

1. Introduction

Recently, group IV alloys such as $\text{Si}_{1-x-y}\text{Ge}_y\text{C}_x$ and $\text{Si}_{1-x}\text{C}_x$ have attracted great attention as new materials for introducing band gap engineering in the present Si technology. Furthermore, the challenge of improving device performance is made possible by the enhancement of transport properties in a MOS channel in strained $\text{Si}_{1-y}\text{Ge}_y/\text{Si}$ structures [1]. We have focused on the tensile strained $\text{Si}_{1-x}\text{C}_x/\text{Si}$ structure since it has several advantages compared to $\text{Si}_{1-y}\text{Ge}_y$. Tensile strained Si films can be formed directly on a Si substrate by adding a few percent of C into the Si films so that a high quality $\text{Si}_{1-y}\text{Ge}_y$ buffer layer is not required. We can select many kinds of non-toxic hydrocarbon gases as a C source for epitaxy of $\text{Si}_{1-x}\text{C}_x$ while GeH_4 , which is usually used as a Ge source in UHV-CVD, is toxic. Furthermore, the thermal conductivity of $\text{Si}_{1-y}\text{Ge}_y$ is inferior to that of Si [2]. In order to demonstrate the advantage of tensile strained $\text{Si}_{1-x}\text{C}_x$ alloys, E. Quinones fabricated a high-mobility

metal-oxide-semiconductor (MOS) devices without using a virtual substrate [3].

Molecular beam epitaxy (MBE) [4] and rapid thermal chemical vapor deposition (RTCVD) [5] techniques have been used to form $\text{Si}_{1-x}\text{C}_x$ alloys at substrate temperatures near 600°C . However, the epitaxial growth of highly C-containing Si layer is very difficult because of the very low solid solubility of C in Si. Hot Wire (HW) Cell method, plasma-enhanced chemical vapor deposition (plasma-CVD) and photochemical vapor deposition (photo-CVD) techniques are widely used for growing thin Si films. These methods allow Si film depositions at very low substrate temperatures ($<300^\circ\text{C}$) [6]. Because of the efficient generation of both SiH_3 radical, having a long life time in the gas-phase, and atomic hydrogen, having an important role of the surface termination, high quality amorphous, polycrystalline and epitaxial Si films were obtained by these methods [7]. In our previous studies, we applied these methods to grow the $\text{Si}_{1-x}\text{C}_x$ alloy on Si(100) and succeeded in obtaining epitaxial $\text{Si}_{1-x}\text{C}_x$ films at a substrate temperature of 200°C [8, 9]. In this paper, we present structural characteristics of the undoped $\text{Si}_{1-x}\text{C}_x$ alloys and electrical characteristics of the phosphorus doped films, which were grown by photo- and plasma-CVD.

2. Experimental Procedure

The mercury-sensitized photo-CVD and rf plasma-CVD methods were used to grow the $\text{Si}_{1-x}\text{C}_x$ films. The reactant gases were SiH_4 and H_2 . We chose three gases, which are C_2H_2 , CH_4 and $\text{SiH}_2(\text{CH}_3)_2$, for *in situ* carbon addition. The total gas pressure during the growth was maintained at 0.5 Torr. Si(001) was used as a substrate. The film thickness and the growth rate were 100-500 nm and 0.02-0.2 nm/s, respectively. The substrate temperature during the growth was maintained at 200°C . *In situ* phosphorus doping was carried out by plasma-CVD using PH_3 . The structure of the films was confirmed by reflection high-energy electron diffraction (RHEED). The optical and structural properties were measured using Raman scattering spectroscopy and a high resolution X-ray diffractometry (HRXRD). The electrical properties were characterized by van der Pauw method.

3. Results and Discussion

In our previous works, we found that the H atoms both in the gas phase and on the growth surface played a very important role in the low-temperature Si epitaxy [10]. We also confirmed the necessity of hydrogen dilution to fabricate the $\text{Si}_{1-x}\text{C}_x$ alloys at the substrate temperature of 200°C [8, 9]. However, the hydrogen incorporation in the films was also found. In order to desorb the H atoms from the films, those were annealed at 700°C in N_2 atmosphere. We confirmed the desorption of H atoms and that the crystallinity of the annealed film remained as a single crystal by RHEED.

It is well known that C atoms located at the substitutional sites of Si network are detected by Raman scattering spectroscopy measurements as the C local vibration mode at 607 cm^{-1} . The Raman scattering spectra of the $\text{Si}_{1-x}\text{C}_x$ films are shown in Fig. 1. The films were grown by photo-CVD with varying $\text{SiH}_2(\text{CH}_3)_2/\text{SiH}_4$ ratio and annealed

at 700°C in N₂ atmosphere. The measurements were carried out at room temperature. The 607 cm⁻¹ mode was detected in the C added samples and the peak intensity depended on the SiH₂(CH₃)₂ addition ratio.

The annealed Si_{1-x}C_x layers were also characterized using X-ray reciprocal lattice space mapping. Fig. 2 illustrates the X-ray reciprocal lattice space map of the diffraction intensity at [115] asymmetric reflection. The peak positions of the annealed Si_{1-x}C_x layer and the substrate were located parallel to the [004] direction. This result reveals that the reduction of the lattice constant occurred only in the direction normal to the surface and not in the in-plane direction. In other words, the Si_{1-x}C_x alloys obtained in this study were strained tensilely.

The substitutional C contents were estimated considering the strain in the films using Vegard's law, which is based on the lattice constants of Si and 3C-SiC. Up to now, the maximum substitutional C content of 3.5 atomic% was successfully obtained by plasma-CVD using SiH₂(CH₃)₂

Fig. 3 shows SIMS profiles of the H and C concentration in the undoped epitaxial films. The film was grown by the plasma-CVD and each layer has different C₂H₂ addition ratio. The sample was annealed at 700°C. It is confirmed that the C content of these films strongly depended on the C₂H₂/SiH₄ ratio. Before annealing, H concentration of the films was about 10²¹cm⁻³ and the value increased with increasing C₂H₂ addition ratio. It suggests that C-H_n bonds are formed in the film. By the annealing, the H concentration is decreased down to 10¹⁹cm⁻³ as shown in Fig. 3. It is noticeable that the C profile after annealing is almost identical to that before annealing, suggesting the small diffusion of C atoms. This is another advantage of the Si_{1-x}C_x/Si system because Ge diffusion under the annealing is one of the problem in Si_{1-y}Ge_y/Si system [11].

We carried out P-doping into Si films by plasma-CVD.

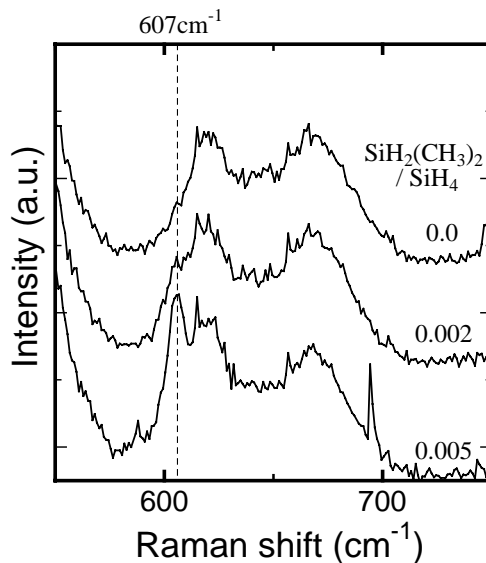


Fig. 1. Raman scattering spectra of the Si_{1-y}C_y films. The films were grown by photo-CVD using SiH₂(CH₃)₂ and annealed at 700°C in N₂ atmosphere.

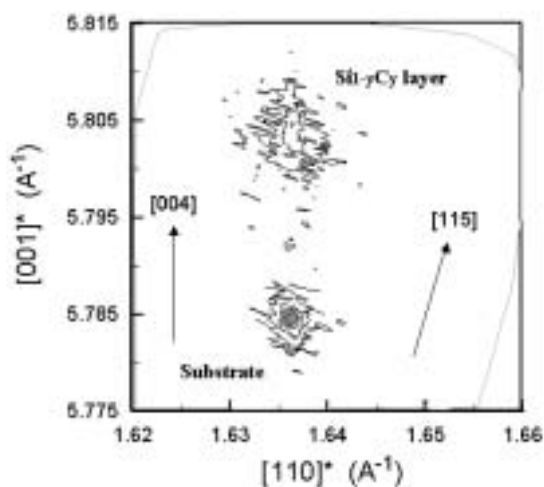


Fig. 2. X-ray reciprocal lattice space map of the diffraction intensity at the [115] asymmetric reflection. The sample was grown by photo-CVD with the C₂H₂/SiH₄ ratio of 0.002 and annealed at 700°C.

The films were grown at the same PH_3/SiH_4 ratio of 0.03%. For the as-grown samples, the electron concentration of $\text{Si}_{1-x}\text{C}_x$ was lower than that of Si. In addition, this tendency became remarkable with increasing addition ratio of $\text{SiH}_2(\text{CH}_3)_2$. However, the value was increased up to the same level of the Si film after annealing at 700°C , which was $5 \times 10^{18} \text{cm}^{-3}$. It means that the dopant neutralization occurred in the as-grown $\text{Si}_{1-x}\text{C}_x$ films and suggests the formation of the complex consisting of P, C and H atoms. The dependence of the electron concentration on the PH_3 doping ratio is shown in Fig. 4. The open and closed circles indicate the films grown with and without $\text{SiH}_2(\text{CH}_3)_2$ addition. The samples were annealed at 700°C . The values of all $\text{Si}_{1-x}\text{C}_x$ films recovered up to the same level of the Si films after annealing. The electron concentration could be controlled ranging from 10^{17}cm^{-3} to 10^{19}cm^{-3} by varying PH_3 doping ratio.

We tried the fabrication of a MOS diode with a $\text{Si}_{1-x}\text{C}_x$ film grown by HW Cell method. The $\text{Si}_{1-x}\text{C}_x$ film ($y=0.005$), with the film thickness of 87nm, was grown on an n-type Si substrate. The SiO_2 film was grown by steam oxidation at 1050°C for 3min, and its thickness was 54nm. Al was deposited as electrodes by evaporation. The area of the electrodes is $1.2 \times 10^{-3} \text{cm}^2$. The C-V characteristics of the MOS diode showed the accumulation, depletion and inversion case with high and low frequency, and the Al- SiO_2 - $\text{Si}_{1-x}\text{C}_x$ diode successfully worked. We are also applying the $\text{Si}_{1-x}\text{C}_x$ films grown by plasma- or photo-CVD with a relatively higher C concentration to the solar cells.

4. Conclusions

We demonstrated the epitaxial growth and characterization of undoped and P-doped $\text{Si}_{1-x}\text{C}_x$ films by photo- and plasma-CVD techniques. We obtained the epitaxial Si films with C_2H_2 , CH_4 or $\text{SiH}_2(\text{CH}_3)_2$ addition to SiH_4 and H_2 gases using both methods at

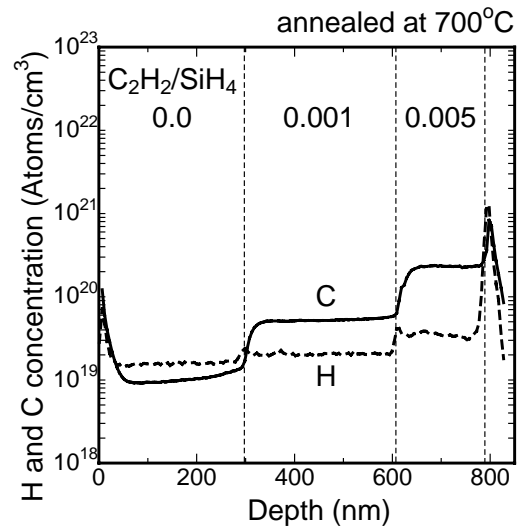


Fig. 3 SIMS profile of the epitaxial film containing three layers. The sample was annealed at 700°C .

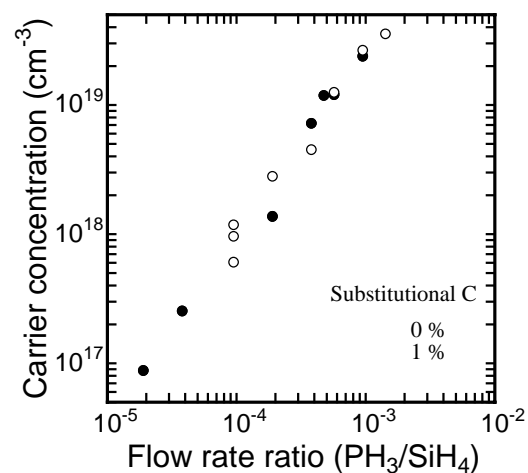


Fig. 4 Dependence of the electron concentration on the PH_3 doping ratio. The samples were grown by plasma-CVD using $\text{SiH}_2(\text{CH}_3)_2$ and annealed at 700°C .

substrate temperature of 200°C. Carbon local vibration mode (607cm^{-1}) in Si network was detected in the samples annealed at 700°C. The pseudomorphic growth of $\text{Si}_{1-x}\text{C}_x$ alloys was confirmed by X-ray reciprocal lattice space mapping. The maximum substitutional C content of 3.5 atomic% was successfully obtained in the films with $\text{SiH}_2(\text{CH}_3)_2$ addition. *In situ* phosphorus doping was carried out by using PH_3 . The dopant neutralization was found in the as-grown $\text{Si}_{1-x}\text{C}_x$ films and the electron concentration increased by the annealing. We succeeded to control the electron concentration ranging from 10^{17}cm^{-3} to 10^{19}cm^{-3} by varying PH_3 doping ratio.

References

- [1] K. Rim, J. L. Hoyt and J. F. Gibbons: IEEE Trans. Electron Dev. **47** (2000) 1406.
- [2] J. P. Dismukes, J. Ekstrom, E. F. Steigmeire, I. Kudman and D. S. Beers: J. Appl. Phys. **35** (1964) 2899.
- [3] E. Quinones, S. K. Ray, K. C. Liu, S. Banerjee, IEEE Electron Device Lett. **20** (1999) 338.
- [4] K. Brunner, W. Winter, K. Eberl, N. Y. Jin-Phillipp, F. Phillipp, J. Cryst. Growth **175/176** (1997) 451.
- [5] P. Boucaud, C. Francis, A. Larre, F. H. Julien, J. -M. Lourtioz, D. Bouchier, S. Bodnar, L. Regolini, Appl. Phys. Lett. **66** (1995) 70.
- [6] K. Nagamine, A. Yamada, M. Konagai, K. Takahashi, Jpn. J. Appl. Phys. **26** (1987) L951.
- [7] K. Abe, T. Tsushima, M. Ichikawa, A. Yamada, M. Konagai, J. Non-cryst. Solids. **266-269** (2000) 105.
- [8] S. Yagi, K. Abe, A. Yamada, M. Konagai, Jpn. J. Appl. Phys. **39** (2000) L1078.
- [9] T. Watahiki, A. Yamada and M. Konagai: J. Crystal. Growth, **209** (2000) 335.
- [10] K. Abe, T. Watahiki, A. Yamada, M. Konagai, Jpn. J. Appl. Phys. **38** (1999) 3622.
- [11] N. Sugii: *New Group IV (Si-Ge-C) Semiconductors: Control of Properties and Applications to Ultrahighspeed and Opto-Electronic Devices*, VI-24, Sendai, Japan, January 21-23, 2001.