Novel Epitaxial Growth Technology of Si$_{1-x}$Ge$_x$ Films
by in situ Rapid Thermal Chemical Vapor Deposition

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The epitaxial growth of Si$_{1-x}$Ge$_x$ has been studied by rapid thermal chemical vapor deposition (RTCVD) to bring this technology close to manufacture. In this paper, a new process which involves in situ substrate treatment with SiH$_4$ will be proposed for forming high quality epitaxial Si$_{1-x}$Ge$_x$ films. Doping characteristics of the film are also discussed.

1. Introduction

In the future generation of Si-based heterostructural devices such as heterobipolar transistor (HBT), epitaxial Si$_{1-x}$Ge$_x$ film becomes of great importance). The electrical characteristics and reliability of the devices will critically depend on the perfection of the epitaxial layer. Thus, the goal of the epitaxial growth of Si$_{1-x}$Ge$_x$ is to obtain the film with controlled Ge concentration and abrupt dopant profiles, and free from dislocation.

Considering commensuration with manufacture and advantage of forming abrupt profiles of dopant and Ge content, we have studied the epitaxial growth of Si$_{1-x}$Ge$_x$ using RTCVD. It is, in general, recognized that surface cleaning or etching has great influence on epitaxy. For instance, high temperature baking in H$_2$ or HCl etching is often used. However, by these methods, the surface may become rough. Thus, in this paper, we will propose a novel epitaxial technology which is effective for decreasing dislocation and smoothing Si$_{1-x}$Ge$_x$ film surface. We will also demonstrate some results of in situ boron doping using B$_2$H$_6$ gas by RTCVD.

2. Experimental

The RTCVD system used consists of a quartz tube, a high vacuum pump and halogen lamps as shown in Fig.1. Si wafers with (100) orientation were cleaned with diluted HF acid, and then Si$_{1-x}$Ge$_x$ films were grown on them from a mixture of SiH$_4$ (10%) and GeH$_4$ (1%) diluted in H$_2$ at temperatures from 700 to 900°C. The reactor pressure was 1x10$^{-5}$ Torr in the base, and 0.1 to 10 Torr in the deposition. Two types of samples were prepared via the processes shown in Table 1. One is that just before Si$_{1-x}$Ge$_x$ deposition, the substrate surface was pretreated, in the reactor, with SiH$_4$ (10%) in H$_2$ at 900°C for a few seconds. The other is that had no SiH$_4$ pretreatment.

The film thickness was evaluated from step height measurements. Film compositions were measured by both Auger electron spectroscopy (AES) and X-ray diffraction for some samples, and both results were in reasonable agreement with each other as shown in Table 2. Accordingly, the composition determined by X-ray diffraction was used in the following discussion. Misfit dislocations and surface morphology of the films were evaluated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The defect density was measured by infrared light laser scanning tomography.

![Fig.1 Schematic drawing of the RTCVD system.](image-url)
Table 1. Preparation sequences employed in this study.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Flow rates</th>
<th>Total pressure</th>
<th>Depo. temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ treatment</td>
<td>1-10</td>
<td>0.1-10</td>
<td>900</td>
</tr>
<tr>
<td>SiGe epi.growth</td>
<td>1-10</td>
<td>0.1-10</td>
<td>700-900</td>
</tr>
</tbody>
</table>

Table 2. Si₁₋ₓ Geₓ film compositions at various temperatures.

<table>
<thead>
<tr>
<th>Depo.temp. (°C)</th>
<th>Thickness (Å)</th>
<th>Ge fraction (%)</th>
<th>XD</th>
<th>AES</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1500</td>
<td>21.2</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>2500</td>
<td>17.6</td>
<td>22.4</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>4000</td>
<td>18.2</td>
<td>17.3</td>
<td></td>
</tr>
</tbody>
</table>

In situ boron doping was made by adding B₂H₆(100ppm) to the SiH₄ and GeH₄ mixture. Profiles of doped boron and other impurities, and carrier concentration profile were determined by secondary ion mass spectroscopy (SIMS) and spreading resistance analysis (SRA), respectively.

3. Results and Discussion

Fig.2 shows cross sectional TEM micrographs of samples #1 (without SiH₄ pretreatment) and #2 (with SiH₄ pretreatment). The film compositions of both samples were the same, 13 % Ge. In sample #1, some misfit dislocations and defects were observed. In addition, a milky surface was formed on sample #1. On the contrary, the cross sectional TEM image of sample #2 indicated dislocation-free Si₁₋ₓ Geₓ/Si interface. As Fig.3 shows, a large amount of dislocations (>10⁶/cm²) was observed in sample #1, but not in sample #2. AFM showed a small undulation of about 500 Å in height on the surface of sample #1, but extremely smaller (<30 Å) undulation on sample #2 as shown in Fig.4. It was also found from an experiment using a partially masked substrate that epitaxial Si layer was formed during the SiH₄ pretreatment.

We have conducted this study on the basis of the ideas that treatment of a Si substrate with a strong reducing agent, SiH₄, must be effective for removing oxides and/or contaminants on the substrate surface by "scrubbing reaction"⁵) and that as a result, high quality epi-Si₁₋ₓ Geₓ film grows on the "cleaned" Si surface.

As anticipated, this SiH₄ pretreatment is quite effective in reducing misfit dislocations and defects. In addition, it is effective in smoothing grown surface. As described above, epitaxial Si layer is formed during the SiH₄ pretreatment. In other words, "scrubbing reaction" and/or epitaxial growth of Si plays a role of improving the quality of epi-Si₁₋ₓ Geₓ film. In view of the fact that epitaxial Si layer requires, at least, a thickness of 500 Å to form a 3000-Å-thick epi-Si₁₋ₓ Geₓ layer with smooth surface, it seems that epitaxial growth of Si plays a more dominant role in this improvement.

Fig. 2 Cross-sectional TEM images of Si₁₋ₓ Geₓ films of samples #1 (a) and #2 (b).

Fig. 3 IR laser scanning tomography images of samples #1 (a) and #2 (b).

Fig. 4 AFM profiles of Si₁₋ₓ Geₓ surfaces of samples #1 (a) and #2 (b).
As shown in Fig. 5, appreciable amounts of O and C atoms were found at the Si$_{1-x}$Ge$_x$/Si interface of sample #2. These atoms were probably introduced from the ambients mainly during the intermission between SiH$_4$ pretreatment and Si$_{1-x}$Ge$_x$ growth. Similar results were also obtained for sample #1. Therefore, they can be diminished by employing an oil-free ultrahigh vacuum system. It is, at the present stage, still uncertain whether these atoms affect the epitaxial growth of Si$_{1-x}$Ge$_x$ or not.

Next, we have attempted in situ boron doping to epi-Si$_{1-x}$Ge$_x$ films by RTCVD. Fig. 6 shows B and Ge profiles in epi-Si$_{1-x}$Ge$_x$ film. A boron doped epi-Si$_{1-x}$Ge$_x$ layer was formed with a uniform Ge profile, and a B profile with abrupt transition width of less than 0.1 um at the Si$_{1-x}$Ge$_x$/Si interface. A very abrupt carrier concentration profile, which is consistent with the SIMS results (Fig. 6), was obtained as shown in Fig. 7.

4. Conclusion

We have developed an epitaxial growth technology of Si$_{1-x}$Ge$_x$ by RTCVD with the optimum process sequence; SiH$_4$ pretreatment and following in situ Si$_{1-x}$Ge$_x$ film growth. This method, which has an ability of precise temperature and ambient controls, gives high quality epitaxial Si$_{1-x}$Ge$_x$ films with abrupt doping profiles and seems to be a hopeful technology for realizing Si-based heterostructural devices. There remains, however, some uncertainties on the origin of the effectiveness of the SiH$_4$ pretreatment. Further studies are in progress.

5. References