Formation of Si Epi./MgO·Al₂O₃, Epi./SiO₂/Si and Its Epitaxial Film Quality

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A new type silicon-on-insulator with Si/MgO·Al₂O₃/SiO₂/Si structure has been developed. MgO·Al₂O₃ (spinel) epitaxial film is grown on (100) Si substrate by chemical vapor deposition. Amorphous SiO₂ is formed by thermal oxidizing Si substrate through spinel film. Si epitaxial film is grown on MgO·Al₂O₃/SiO₂/Si by SiH₄ pyrolysis. Strain-free Si epitaxial film is attained. Si film Crystalline quality evaluated by X-ray rocking curve is equivalent to that in SOS.

1. Introduction

Many silicon on insulator (SOI) crystal growth techniques, including silicon on sapphire (SOS) and laser beam annealing Si film recrystallization on amorphous insulator, are under development for the fabricating more densely integrated and higher speed MOS devices, high-voltage integrated circuits and so on.

Of these techniques, double-heteroepitaxial SOI with epitaxial-Si / epitaxial-insulator/Si substrate structure has a marked advantage, in that a large area SOI is easily attained by growing insulator and Si epitaxial films on the whole surface of Si substrate. Several insulators, such as MgO·Al₂O₃ (spinel) and CaF₂ have been investigated in this technique (1)~(6). Spinel is noticable material, because it results in better Si device properties, compared with SOS, due to smaller lattice constant mismatch with Si and less impurity contamination (7, 8).

Using spinel epitaxy, Si thermal oxidation and Si epitaxy, we have developed a new type SOI having Si/spinel/SiO₂/Si structure, in which Si epitaxial film is strain-free. Thermal oxidized SiO₂ is a high quality insulator with low dielectric constant. Therefore, this SOI is expected to be more useful for device application than Si/spinel/Si. In this work, spinel hetero-epitaxial growth and Si/spinel/SiO₂/Si formation techniques are presented.

2. MgO·Al₂O₃ Epitaxial Growth

Insulator hetero-epitaxy on Si substrate is a key technique for achieving double hetero-epitaxial SOI. In our case, spinel epitaxial growth was carried out by chemical vapor deposition (CVD). Fig. 1 shows a CVD reactor and the interrelation between gas species transported. The reactor was improved over the reactor which had been developed for Y₃Fe₅O₁₂ epitaxial growth (9). MgCl₂-AlCl₃-CO₂-H₂-N₂ gas system was used in which N₂ gas was the carrier gas. Al is transported as AlCl₃, which is formed by the reaction between Al and HCl. Both MgCl₂-AlCl₃ and CO₂-H₂, which are independently transported with N₂ gas, are mixed in the growth chamber. The epitaxial growth occurs on the (100) Si substrate due to the following reaction.

\[
\text{N}_2 + \text{H}_2 + \text{CO}_2 \rightarrow \text{MgCl}_2 + \text{AlCl}_3 + \text{CO}_2 + \text{N}_2
\]

Fig. 1 CVD reactor for MgO·Al₂O₃ epitaxial film growth.
\[
\text{MgCl}_2 + 2\text{AlCl}_3 + 4\text{CO}_2 + 4\text{H}_2 \rightarrow \text{MgO·Al}_2\text{O}_3 + 4\text{CO} + 8\text{HCl}
\]

Table 1 shows the epitaxial growth conditions.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Transport rate</th>
<th>Flow rate</th>
<th>Growth temperature</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.3-0.8 g/hr</td>
<td>100-500 CC/min</td>
<td>850-1050 °C</td>
<td>Si (100)</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>6.0-11.0 g/hr</td>
<td>20 I/min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO²</td>
<td>56 I/min</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td></td>
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</tbody>
</table>

![X-ray diffraction pattern](image)

Fig. 2 MgO-Al₂O₃ X-ray diffraction pattern for 0.4 μm thick epitaxial film. (a) θ-2θ mode chart (b) (400) X-ray rocking curve.

In order to evaluate the epitaxial film crystalline quality, θ-2θ mode X-ray charts and double-crystal X-ray rocking curves (XRC) were obtained as shown in Fig. 2. Only the (400) diffraction peak was observed with strong intensity in θ-2θ mode. Half value widths (HVW) of (400) XRC were from 0.75 to 1.0 degrees for 0.4 μm thick epitaxial films grown under the optimum growth conditions. The film crystalline quality became inferior as the thickness decreased because HVW increased. HVW was about 1.8 degrees for 0.1 μm thick films.

From a practical production view-point, it is necessary that film thickness and quality uniformities are achieved in the large growth area. For films grown on four 3-inch substrates in the same run, the film thickness distribution was within ±3% and the (400) XRC HVW was almost the same. The growth rate is limited to the surface reaction, whose activation energy is 1.0 ev.

3. Si/MgO-Al₂O₃/SiO₂/Si Formation

A thicker insulator is desirable in the Si/Insulator/Si for the fabricating completely isolated and higher speed devices. However, there are problems inherent in growing thick spinel. One problem is the low growth rate, which is about 0.5 μm/hr. The other inevitable problem is crack formation in the thick spinel film due to the difference in thermal expansion coefficient between spinel and Si. Fig. 3 shows a crack which was induced in the 0.8 μm thick film grown at 980 °C. <100> crack lines indicate that the spinel film is single crystal.

![Crack lines](image)

Fig. 3 Crack lines induced in MgO-Al₂O₃ epitaxial film.

In order to solve the above problems, a new SOI having a Si/spinel/SiO₂/Si structure has been developed. Fig. 4 shows the formation process. After spinel epitaxial growth, SiO₂ is formed between spinel film and Si substrate by thermal oxidizing the Si substrate through spinel film. Finally, Si epitaxial film is grown on spinel epitaxial film by SiH₄ pyrolysis in H₂ at 1030 °C, using a vertical reactor.

Thermal oxidation for SiO₂ formation was performed in a wet O₂ ambient. Film thickness and refractive index were measured by optical interference method and ellipsometry. About 0.5 μm thick amorphous SiO₂ was formed by 1.5 hours thermal
oxidation at 1100 °C in wet O₂ ambient. Refractive index was 1.45 which is in accord with the wellknown value of SiO₂. Fig. 5 shows a cross section view of Si/spinel/SiO₂ in which SiO₂ is observed as a black layer.

![Diagram of MgO·Al₂O₃ epilayer growth](image)

1. **MgO·Al₂O₃ epilayer growth**

2. **Thermal oxidation**

3. **Si epitaxial growth**

Fig. 4 Formation process of Si/MgO·Al₂O₃/SiO₂/Si.

![SEM image of Si/MgO·Al₂O₃/SiO₂/Si](image)

Fig. 5 Cross section view of Si/MgO·Al₂O₃/SiO₂/Si by SEM.

Fig. 6 shows XRC of spinel symmetric (400) and Si asymmetric (422) diffractions. Fig. 6-(a) and (b) are spinel (400) XRC, which were observed in the stages of spinel/Si and Si/spinel/SiO₂/Si, respectively. Spinel epitaxial film quality was improved in the thermal oxidation process, in which HVW was reduced from 1.8 to 1.3 degrees. Fig. 6-(c) shows Si (422) XRC for Si/spinel/SiO₂/Si having 0.1 μm thick spinel and 0.5 μm thick SiO₂. It consists of a sharp top and broad skirt parts which correspond to diffractions from Si substrate and Si epitaxial film, respectively. The Si epitaxial film crystalline quality, therefore, can be evaluated from HVW of the broad skirt part. HVW of 3.0 μm thick Si epitaxial film was 0.35 degrees, while it was 0.2 degrees in Si/spinel/Si having the same Si and spinel film thicknesses.

![X-ray rocking curve of MgO·Al₂O₃ (400) and Si asymmetric (422) diffractions](image)

Fig. 6 X-ray rocking curve of MgO·Al₂O₃ (400) and Si asymmetric (422) diffractions for MgO·Al₂O₃/Si and Si/MgO·Al₂O₃/SiO₂/Si in the case of 0.1 μm thick spinel and 0.5 μm thick SiO₂.

The Si epitaxial film thickness dependence of Si (422) XRC HVW was investigated for Si/spinel/SiO₂/Si and Si/spinel/Si in the range of Si film thickness of 0.6 ~ 3.0 μm as shown in Fig. 7. HVW were level equivalent to SOS. However, it became larger in Si/spinel/SiO₂/Si than in Si/spinel/Si in spite of the spinel crystalline quality being improved in the former structure as mentioned above. This indicated that, in addition to spinel epitaxial crystalline quality, there are several factors to dominate the crystalline quality of Si epitaxial film (6). The slight Si epitaxial film quality inferiority in Si/spinel/SiO₂/Si may be improved by some techniques, such as Si epitaxial growth optimizations. Si/spinel/SiO₂/Si is expected to be rather more useful for device applications than Si/spinel/Si because the thermal oxidized SiO₂ is a high quality insulator with low dielectric constant.
4. Conclusion

A new type SOI having Si/spinel/\(\text{SiO}_2\)/Si structure has been developed. Spinel epitaxial films were grown on (100) Si substrate by CVD, using newly-designed horizontal reactor and MgCl\(_2\)-Al-HCl-Co\(_2\)-N\(_2\) gas system. Excellent uniformities of film thickness and crystalline quality were obtained. \(\text{SiO}_2\) was formed by thermal oxidizing Si substrate through spinel film after growing spinel film. This SOI has solved the problem regarding strain induced in the Si epitaxial film, which was inevitable when using other SOI techniques. No strain was observed by either XRC or Raman spectroscopy.

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Insulator hetero-epitaxial SOI is expected to attain strain-free Si epitaxial film because there is no difference in thermal expansion coefficient between Si epitaxial film and substrate. The strain induced in Si epitaxial film should shift the film diffraction peak from that for the substrate in Si XRC. Both the substrate and film diffraction peaks of Si (422) XRC shown in Fig. 6-c) were overlapped at the same diffraction angle. This indicates that Si epitaxial film grown on spinel/\(\text{SiO}_2\)/Si substrate is strain-free. The strain-free epitaxial film was also ascertained by Raman spectroscopy. The Raman shift spectrum which appears at 521 cm\(^{-1}\) for bulk Si was observed at the same position for the Si/spinel/\(\text{SiO}_2\)/Si.

For Si/spinel/Si, the same results were obtained for 0.1 \(\mu\)m thick spinel. However, for 0.4 \(\mu\)m thick spinel, the slight compressive strain of about 4x10\(^{-4}\), which is one tenth that for SOS, was observed in both XRC and Raman spectroscopy.

Fig. 7 Si epitaxial film thickness dependence of Si(422) X-ray rocking curve half value width for Si/MgO/Al\(_2\)O\(_3\)/\(\text{SiO}_2\)/Si and Si/MgO/Al\(_2\)O\(_3\)/Si in the case of 0.1 \(\mu\)m thick spinel and 0.5 \(\mu\)m thick \(\text{SiO}_2\).

\(\text{Si/MgO-Al}_2\text{O}_3/\text{SiO}_2/\text{Si}

\(\text{Si/MgO-Al}_2\text{O}_3/\text{Si}

Si film thickness (\(\mu\)m)