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Oxide Mediated Solid Phase Epitaxy (OMSPE) of Silicon: A New Low Temperature Epitaxy Technique Using Intentionally Grown Native Oxide

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1. Introduction

It is well recognized that even a small amount of oxygen atoms on Si substrates causes defects in epitaxial Si layers. Thus, *in-situ* native oxide removal step, such as H_2 bake at high temperatures, has to be performed.[1] Otherwise, careful attentions have to be paid in order to prevent the reoxidation prior to the epitaxy.[2]

In this paper, a new low temperature epitaxial technique is proposed, which makes use of the native oxide on the Si surface. An epitaxial Si layer having good quality can be obtained using SPE (solid phase epitaxy), mediated by an intentionally grown native oxide layer on the Si substrate. Mechanism and applications of this new epitaxial technique will also be shown.

2. Experiment

Experimental procedure is shown in Fig.1. (001) Si substrates were dipped in the HF solution. Then the native oxide was intentionally grown by exposing the substrates to the atmosphere. Exposure time between HF dipping and the loading into the chamber was changed for the various thickness of native oxide. Amorphous Si films were deposited without any *in-situ* cleaning. Undoped amorphous films with the thickness of 200 nm were deposited using Si_2H_6 as a source gas, at 480°C with the pressure of 0.3 Torr. The deposited samples were then annealed in a nitrogen ambient at 600°C for 3 hours, which is sufficient for the crystallization by SPE. The crystallinity of the films was examined by TEM. The oxygen concentration at the interface between the Si substrate and the deposited film was measured by SIMS.

Interfacial oxygen concentration could be controlled by the exposure time as shown in Fig.2. Oxygen coverage is also shown, defining that 1ML is equivalent to 1.36E15cm^{-2} which is the number of back-bonds on the surface of (001) Si substrates.

3. Epitaxial Growth Mediated by Oxide

The crystallinity of the films, deposited in amorphous phase with the adequate native oxide and crystallized by SPE, showed quite interesting features. Figure 3 shows a cross-sectional TEM image of the sample with the interfacial oxygen concentration of 3.3E14cm^{-2}. No defect was observed in the deposited layer, even though the oxygen atoms were detected at the interface.

In case of the usual epitaxial growth, VPE (vapor phase epitaxy) in which the film is deposited in crystalline phase, just a small amount of oxygen causes defects such as twins, as shown in Fig.4, where the oxygen concentration was only 3E13cm^{-2}. As is shown in Fig.4, it is natural that the epitaxial layer has defects due to the interfacial oxygen. Higher oxygen concentration always induces higher defect concentration.

On the contrary, single crystal without defects could be grown using SPE in spite of the high oxygen concentration, as shown in Fig.3. This suggests that the interfacial oxygen has an important role on the epitaxial growth, like the oxide mediated epitaxy (OME) of cobalt silicide[3]. Thus, it was named as oxide mediated SPE (OMSPE) of Si.

The crystallinity dependence on the interfacial oxygen concentration indicates that adequate oxygen concentration is required for OMSPE. Typical TEM images of the samples with smaller amount (1.7E14cm^{-2}) and larger amount (5.8E14cm^{-2}) of oxygen are shown in Fig.5 (a) and (b), respectively. Defects were observed in both cases, but the structures were different. Dislocations with rough surface were seen in Fig.5 (a), and twins were observed in Fig.5 (b).

4. Mechanism of OMSPE

The detailed investigation in case of the small amount of interfacial oxygen suggests the mechanism of OMSPE. Figure 6 shows the TEM image for the as-deposited sample with oxygen concentration of 1.7 E14cm^{-2}. It can be shown that the deposited layer was partly crystallized epitaxially and the rest was amorphous. This was due to the local distribution of the too small amount of oxygen which inhibited the epitaxial growth. Dislocations originated from the sites where the oxygen atoms were localized. Partial crystallization during the deposition also brought about the surface roughness because of the difference of the deposition rate on the single crystal region and on the amorphous region.

With the adequate amount of oxygen at the interface, the fast and local crystallization was suppressed by the mediation of the native oxide. Thus, the uniform epitaxial growth during SPE can be realized and no defect was formed. The dependence of the crystallinity on the interfacial oxygen concentration is summarized in Table I, which was obtained from TEM observations for the samples with various concentration of oxygen. The adequate amount of oxygen is equivalent to about 0.2-0.3 ML. Figure 7 shows the schematic illustration of (001) Si surface with 0.25 ML of oxygen. Such amount of oxygen prevents the epitaxial growth during the deposition, but does not prevent the growth during SPE. This oxygen layer has a role of uniformly slowing down the SPE rate and of keeping the growth-front parallel to the (001) surface.

5. Application of OMSPE

OMSPE can be used as one of the low temperature selective epitaxial technique as shown in Fig.8. Amorphous Si film was conformally deposited and only the region deposited on Si surface was crystallized by the subsequent annealing. Amorphous area can be selectively removed by HF/HNO_3 acid.

6. Conclusion

OMSPE of Si was developed as one of the low-temperature unique epitaxial growth technique. Single crystalline layers without defects can be grown on Si substrates mediated by the adequate concentration of oxygen of about 0.2-0.3 ML. It was demonstrated for the first time that the native oxide can be positively used for the epitaxial growth.

1) T.O.Sedgwick et al.: Appl. Phys. Lett. **54**, 2689 (1989).
2) B.S.Meyerson: Appl. Phys. Lett. **48**, 797 (1986).
3) R.T.Tung: Appl. Phys. Lett. **68**, 3461 (1996).

- (001) Si substrate
- HF dipping
- Exposure to atmosphere for native oxide growth, Temp: 24°C, Humidity: 45%
- Loading to CVD chamber
- Deposition of a-Si (Si_2H_6, 480°C)
- Annealing in N_2 for crystallization (600°C, 3 hours)
- Characterization (TEM, SIMS, etc.)

Fig.1 Experimental procedure.

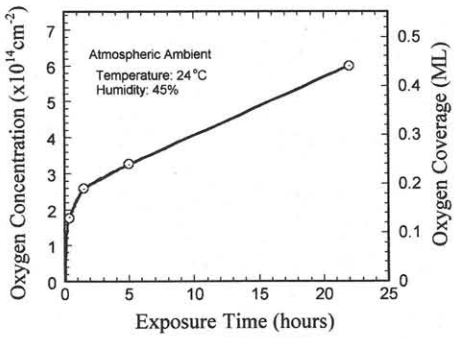

Fig.2 Dependence of oxygen concentration at the interface on the exposure time to the atmosphere. Oxygen coverage is also shown. This indicates that the native oxide can be controlled intentionally.

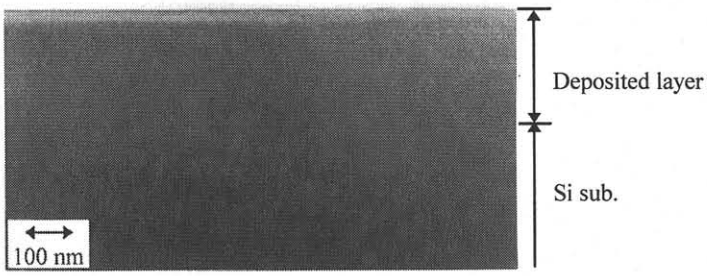

Fig.3 Cross-sectional TEM image of OMSPE sample with the interfacial oxygen concentration of 3.3E14cm^{-2}. No defect is observed in the OMSPE layer.

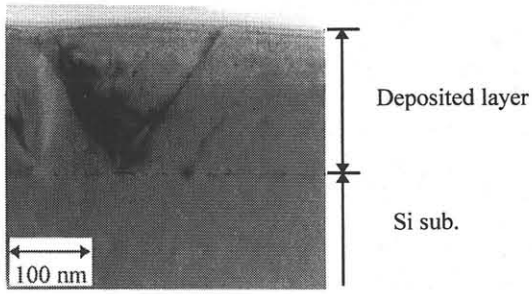

Fig.4 Cross-sectional TEM image of VPE sample with the oxygen concentration of 3E13cm^{-2}. In spite of much lower concentration than that shown in Fig.3, defects are observed in the deposited layer.

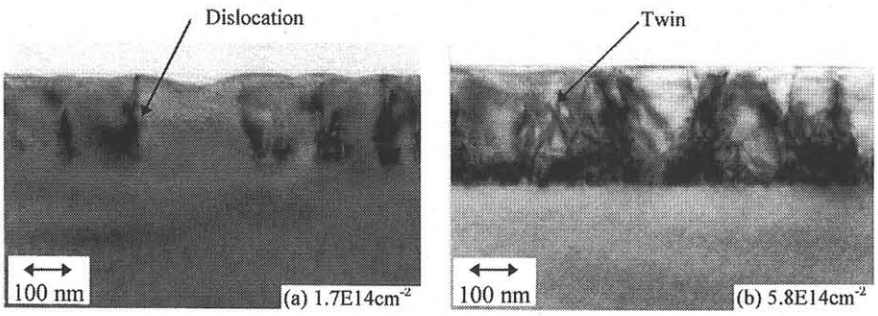

Fig.5 Cross-sectional TEM images of OMSPE samples with the (a) lower and (b) higher interfacial oxygen concentration than the sample with adequate oxygen concentration as shown in Fig.3.

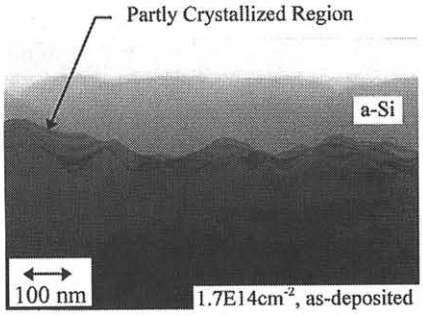

Fig.6 Cross-sectional TEM image of the as-deposited sample with low oxygen concentration as shown in Fig.5(a). Some part of the deposited amorphous was already crystallized.

Table I. Dependence of the crystallinity obtained by OMSPE on the interfacial oxygen concentration. Critical concentrations were determined by TEM observation for samples with various interfacial oxygen concentration.

Interfacial Oxygen Concentration (Coverage)	~2.7 x10^{14}cm^{-2} (~0.2 ML)	2.7~4.1 x10^{14}cm^{-2} (0.2~0.3 ML)	4.1 x10^{14}cm^{-2}~ (0.3 ML ~)
Crystallinity in the deposited layer	dislocation	no defect	twin
Cross-sectional TEM image of OMSPE Sample	Fig.5 (a)	Fig.3	Fig.5 (b)

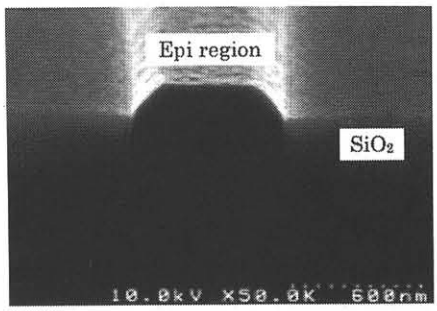

Fig.8 Application to selective epitaxy. Amorphous Si was conformally deposited and only the area on Si substrate was crystallized by OMSPE. Then, amorphous region on SiO_2 was selectively etched.

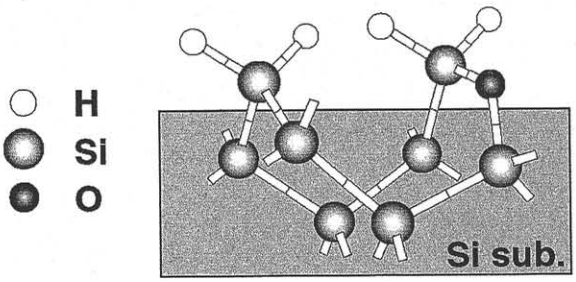

Fig.7 Atomic model of the (001) Si surface with 0.25 ML of oxygen. Such amount of oxygen prevents the epitaxial growth during deposition, but does not prevent the growth during SPE.