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Thermally Stable $TiSi_2$ Thin Films by Modification in Interface and Surface Structures

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A novel method to improve the thermal stability of TiSi2 thin films has been developed. This improvement is achieved by the combination of two treatments; sputter-etching prior to Ti deposition and oxidation of TiSi2 films. It is found that these two treatments form the additional layers which contain oxygen at TiSi2/Si interface and TiSi2 surface, respectively. These layers would suppress the agglomeration during high temperature annealing by retarding movement of Ti and Si atoms at the TiSi2/Si interface and TiSi2 surface.

1. INTRODUCTION

TiSi2 formed by thermal reaction between Ti and Si is the most attractive candidate for self-aligned silicide (salicide) application. However, it has been previously reported that the TiSi2 thin film suffers increase in sheet resistance and degradation of surface morphology due to agglomeration during high temperature annealing.[1),2)] This phenomenon affects both the shallow junction integrity and MOS integrity when TiSi2 is formed on diffused layers or polycrystalline silicon gate electrodes, respectively.[1)]

Agglomeration occurs due to movement and rearrangement of Ti and Si atoms to minimize the TiSi2 surface or TiSi2/Si interface energies. In a kinetic viewpoint, atomic movement may be caused by high surface and interface mobility of Ti and Si atoms. Therefore, the agglomeration phenomenon might be sensitive to surface and interface structures of TiSi2 films.

In this paper, a novel method to improve the thermal stability of TiSi2 films has been proposed. This improvement has been achieved by modification of the surface and interface structures of TiSi2 films.

2. EXPERIMENTAL PROCEDURE

The process sequence is shown in Fig.1. P-type Si wafers were dipped in a buffered HF solution to remove native oxide. These wafers were divided in two sets. For one set of wafers, in-situ Ar^+ sputter-etching was performed and 35-nm Ti films were deposited by using a sputtering method. For the other set of wafers, sputter-etching prior to Ti deposition was not carried out. Two step LA

- P-type Si wafers
- Buffered HF dip
- <In-situ Ar^+ sputter-etching>
- 35nm Ti deposition
- 1st LA in N2
- Selective etch of Ti and TiN
- 2nd LA in N2
- LTO deposition(100nm)
- <Oxidation at 850°C for 30min in O2>
- Annealing in N2 at 850°C-950°C

Fig.1 Process sequence. Steps denoted by < > were carried out for separate batch of wafers.

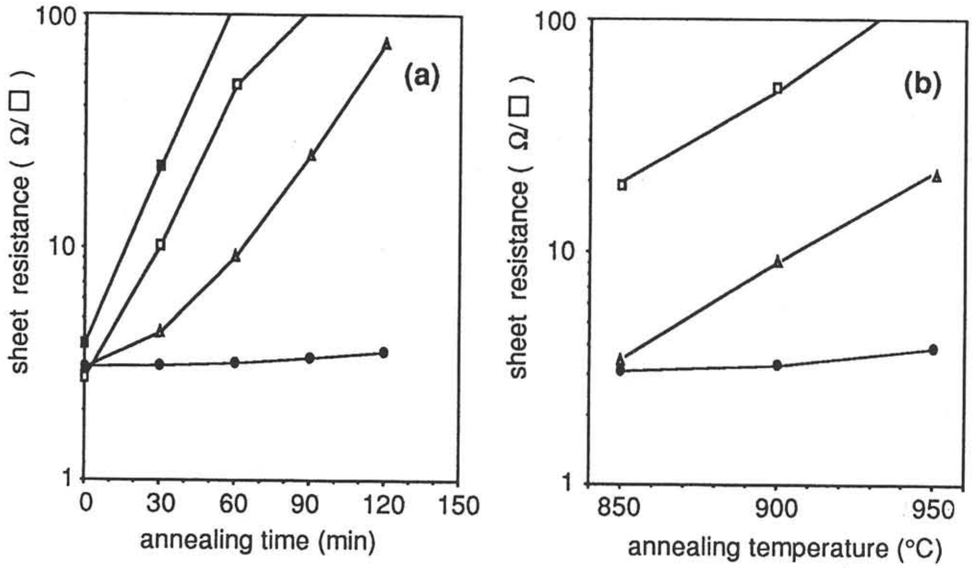

Fig.2 Increase in sheet resistance of TiSi2 films as a function of (a) annealing time at 900°C in N2 and (b) annealing temperature for 60min in N2.

	sputter-etching	oxidation
-■-	×	○
-□-	×	×
-▲-	○	×
-●-	○	○

(lamp annealing), which was usually used in a salicide formation[3], was carried out. This annealing resulted in formation of 48-nm TiSi2 films with sheet resistance of 3 Ω/□. Subsequently, all samples were covered with low temperature CVD oxides (LTO) and some samples were oxidized at 850°C in O2 for 30min. In order to evaluate the thermal stability of the TiSi2 films, all samples were annealed in N2 ambient at 850°C-950°C.

3. RESULTS AND DISCUSSION

Figure 2 shows dependence of TiSi2 sheet resistance on annealing time and temperature in N2. These results show that the following two treatments have a remarkable relation to the thermal stability of TiSi2 films.

(1) Effects of sputter-etching

Sheet resistance of TiSi2 films without sputter-etching prior to Ti deposition begin to increase at 850°C. Figure 3 shows cross sectional SEM (scanning electron microscopy) photographs of TiSi2 films after annealing at 900°C for 120min. When sputter-etching is not carried out, serious agglomeration is observed. It is interesting that the isolated clusters of the TiSi2 film sink into the substrate rather than into LTO. This fact indicates that Si atoms in a substrate also move during the agglomeration process.

Sputter-etching is found to be effective in suppressing agglomeration and increase in sheet resistance (see Fig.2 and Fig.3). In order to investigate mechanisms of the improvement by sputter-etching, characteristics of TiSi2 films were examined by XRD (X-ray diffraction), SIMS (secondary

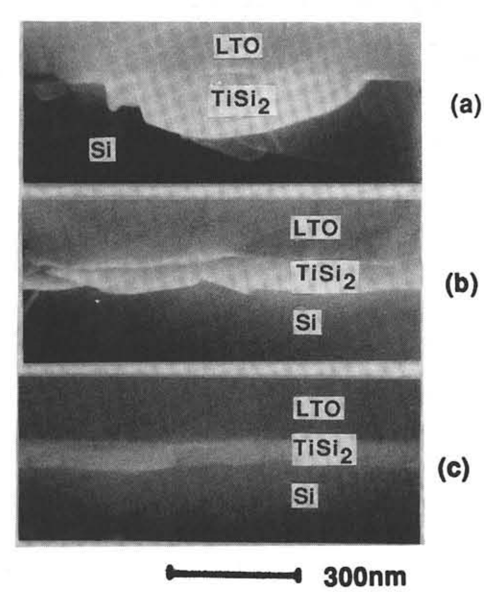

Fig.3 Cross sectional SEM photographs after annealing at 900°C for 120min in N2. (a) without sputter-etching, (b) with sputter-etching prior to Ti deposition, and (c) with sputter-etching and oxidized at 850°C for 30min after LTO deposition.

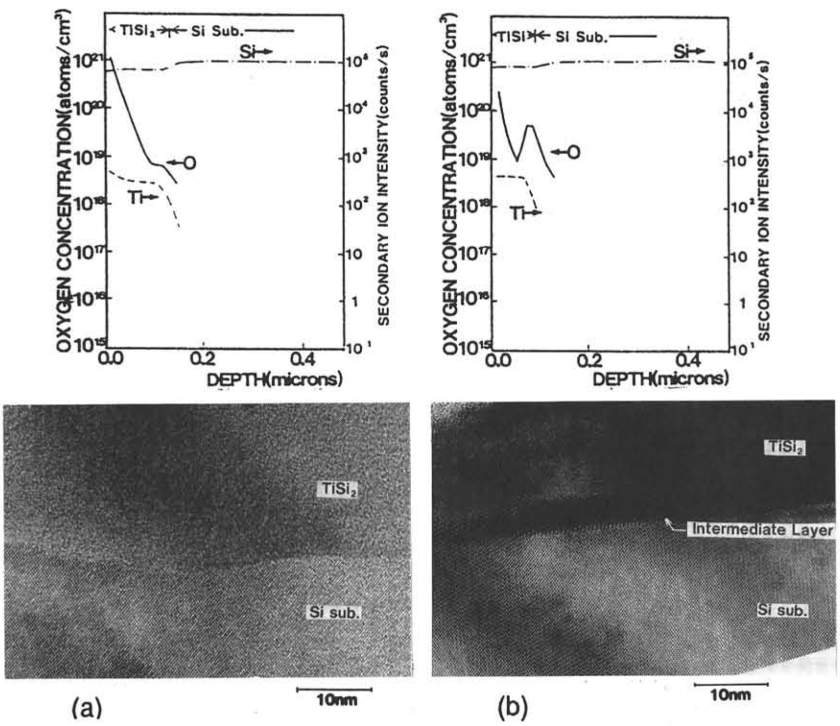

Fig.4 SIMS depth profiles and cross sectional TEM micrographs of TiSi2 films. (a)without sputter-etching,and (b)with sputter-etching prior to Ti deposition.

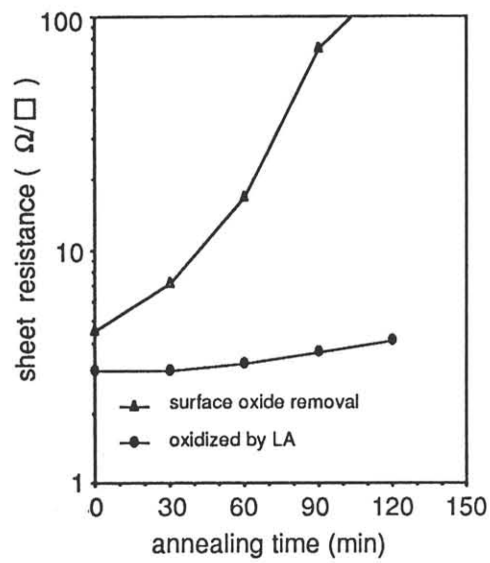

Fig.5 Sheet resistance of TiSi2 films as a function of annealing time at 900°C in N2.

ion mass spectrometry) and cross sectional TEM(transmission electron microscopy). No difference was observed in XRD spectra between TiSi2 films with and without sputter-etching. However , only in the TiSi2 film with sputter-etching, a crystalline intermediate layer is observed at the TiSi2/Si interface by TEM analyses, and this layer contains oxygen atoms with a concentration of about 10^{20} atoms/cm^3, as shown in Fig.4(b). From these results, a possible mechanism of improvement is that this intermediate layer suppresses the movements of Ti and Si atoms at TiSi2/Si interface and/or change the interface energy of the TiSi2/Si interface.

(2) Effects of O2 annealing

Further improvement has been achieved by oxidation of TiSi2 in O2. Increase in sheet resistance after annealing is fairly small and the morphology of the TiSi2 film is drastically improved(see Fig.2 and Fig.3).

Table 1 Dependence of TiSi2 sheet resistance on oxidation temperature.

oxidation conditions	before oxidation	after oxidation	after 900°C 120min
NO	3.01	---	75.80
800°C,30min	3.01	3.01	3.77
850°C,30min	3.10	3.10	3.61
900°C,30min	3.05	3.13	3.79
950°c,30min	3.05	3.16	3.92

(Ω/□)

Table 1 shows dependence of the improvement effects on oxidation temperature. It is found that oxidation of TiSi2 at 800°C-950°C successfully prevents increase in sheet resistance after annealing. It should be noticed that this improvement in thermal stability is able to be achieved by combining sputter-etching and oxidation(see Fig.2). This fact indicates that the control of the TiSi2/Si interface is still necessary for the improvement by oxidation.

In order to investigate the mechanism of the improvement in more detail, a following experiment was carried out. TiSi2 films were directly oxidized at 900°C for 90sec in O2 by using the LA method. For some samples, the surface oxide layers were removed by a RIE(Reactive Ion Etching) method after LA. Subsequently, all wafers were covered with LTO and annealed at 900°C in N2 to examine the thermal stability. In Fig.5, sheet resistance of TiSi2 films as a function of annealing time is shown. The samples directly oxidized have excellent thermal stability, whereas degradation occurs in the samples without surface oxide layers. The ESCA(electron spectroscopy for chemical analysis) spectra from the surfaces of the samples before and after oxidation, are shown in Fig.6. In the case of the oxidized sample, peaks from not only SiO2 but also TiOx are detected, and thickness of the surface oxide layer is estimated to be about 110Å. From results of angular dependence in ESCA spectra, it was found that contents of TiOx increase near the oxide/TiSi2 interface.

These results indicate that existence of the surface oxide (particularly TiOx) layer would retard movement of Ti and Si atoms at the TiSi2 surface, and consequently would suppress the agglomeration during high temperature annealing.

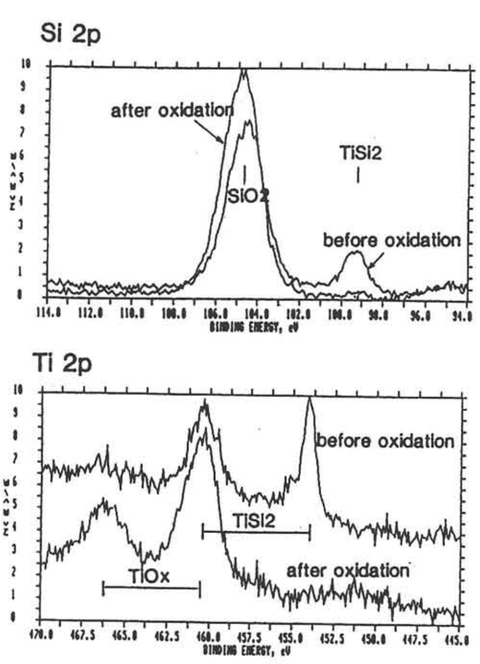

Fig.6 ESCA spectra from the surfaces of samples before and after oxidation. The oxidation was carried out at 900°C for 90sec in O2.

4. CONCLUSIONS

A drastic improvement in thermal stability of the thin TiSi2 films has been achieved by combination of two treatments; sputter-etching prior to Ti deposition and oxidation of TiSi2. It is found that sputter-etching prior to Ti deposition causes formation of the intermediate layer with oxygen at the TiSi2/Si interface. On the other hand, the surface oxide layer with SiO2 and TiOx on TiSi2 layer is formed by oxidation of TiSi2. These two layers would suppress progress of the agglomeration of TiSi2 by retarding movement of Ti and Si atoms at the TiSi2 surface and the TiSi2/Si interface.

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