

Self-Aligned Silicidation of Zr and its Comparison with Ti

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This paper demonstrates that Zr is a metal more suitable to self-aligned silicidation than Ti which is widely studied for VLSI production. A zirconium silicide layer is reproducibly formed even if a thin silicon oxide film exists on a silicon substrate. Self-aligned silicidation of Zr results in much less lateral over-growth, smoother surface, and more sharp pattern than that of Ti.

1. Introduction

In order to fabricate submicron devices, self-aligned silicidation of source/drain and gate regions of MOS transistors is greatly remarked. Self-aligned silicidation of Ti is expected to be the most promising candidate to reduce sheet resistance of diffusion and poly-silicon layers of MOS transistors (1,2,3). This process, however, results in a rough surface and rapid lateral over-growth of a titanium silicide layer due to high thermal stress and high diffusivity of Si.

The authors have selected ZrSi_2 to solve the above problems. Because of the chemical activity of Zr, ZrSi_2 is formed by lower energy than TiSi_2 (4). Thermal stress of a ZrSi_2 film might be reduced because the volume change in silicide formation of Zr is less than that of Ti (5). Also, Low resistance metallization can be achieved because ZrSi_2 has lower work function than TiSi_2 and low resistivity.

This paper describes self-aligned silicidation of Zr and demonstrates some advantages of ZrSi_2 over TiSi_2 .

2. Experiment

Zirconium films were deposited on chemically-cleaned p-type, (100)-oriented silicon substrates by DC magnetron sputtering. Sputtering was done in argon ambient of 0.4 Pa. The deposition rate was 130 nm/min. Silicidation reactions were done by annealing at temperature from 600 to 1000°C in H_2 -Ar ambients. The silicide films formed by annealing were characterized using X-ray diffraction and AES. The sheet resistance was

measured by the four-point probe technique.

3. Results and discussions

(1) Formation and characterization of zirconium silicide

Figure 1 shows the sheet resistance as a function of the annealing temperature. Annealing was done in 5% H_2 -Ar ambients for 30 min. At temperatures above 600°C, silicide formation causes the sheet resistance to decrease as the temperature increases. These results agree with those in S.P. Murarka's report (4). For IV_A and V_A group transition metals, the sheet resistance vs. annealing temperature shows the similar

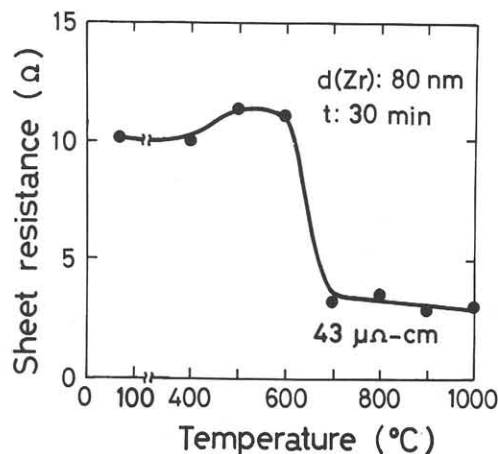


Figure 1 Sheet resistance vs. annealing temperature.

dependence. The resistivity of zirconium silicide is about 4.3×10^{-5} ohm-cm.

Figure 2 shows sheet resistance vs. the ratio of hydrogen gas volume to the total ambient gas volume. Annealing was done at three temperatures for 20 min. As this figure shows, sheet resistance decreases abruptly at the ratio of near 0.5%. Above 0.5%, as the ratio of hydrogen gas increases, sheet resistance decreases gradually. It is clear that hydrogen in the annealing ambient is effective for the zirconium silicidation.

The phase of zirconium silicide were identified by X-ray diffraction technique. Figure 3 shows X-ray diffraction spectra from the samples annealed at 650°C. As the annealing time increases, the peaks from α -Zr metal disappear and the peaks from ZrSi_2 appear. The ZrSi_2 peaks become dominant at a long annealing time. The composition of zirconium silicide was also estimated to $\text{Zr}:\text{Si}=1:2$ by AES (5). These results indicate that zirconium silicide formed by thermal reaction is stoichiometric ZrSi_2 .

(2) Formation process of zirconium silicide

Two types of samples were prepared to investigate the influence of interfacial SiO_2 on the silicidation reaction. One was a bare silicon substrate etched by HF solution, and the other was a silicon substrate covered with a SiO_2 film by boiling in HNO_3 solution. Then, a Zr film was deposited on the each substrate by sputtering. The silicide was formed by annealing at 670°C in 5% H_2 -Ar ambients. Figure 4 shows sheet resistance vs. annealing time. In Figure 4, (a) and (b) show results from bare silicon substrates and silicon substrates covered with a SiO_2 film, respectively. For bare silicon substrates (a), the sheet resistance decreases as the annealing time increases, zirconium silicide forms after annealing for 18 min. For silicon substrates covered with a SiO_2 film (b), the silicide formation is delayed by the presence of interfacial SiO_2 film. However, after adequate annealing, the sheet resistance for (b) is equal to that for (a). The heat of formation per oxygen atom of oxide of Zr and Si is about -130 kcal and -70 kcal (7). The oxide of Zr is more stable than that of Si. Therefore, it is considered that Zr can reduce SiO_2 and this reaction enables silicide to form even if a thin SiO_2 film remains.

Figure 5(a) and (b) shows the depth profiles of Zr/Si systems without annealing and after annealing at 670°C in 5% H_2 -Ar ambients for 45 min, respectively, which were obtained from AES analysis. The silicon substrates were etched by HF

solution, and Zr films were deposited on them. Before annealing, thickness of initial Zr films is 29 nm. As is shown in Figure 5(a), there is a group of oxygen before annealing which probably forms zirconium oxide in side of the Zr film near

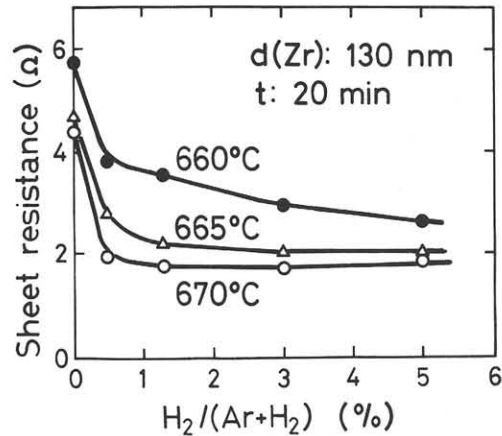


Figure 2 Sheet resistance vs. $\text{H}_2/(\text{Ar}+\text{H}_2)$.

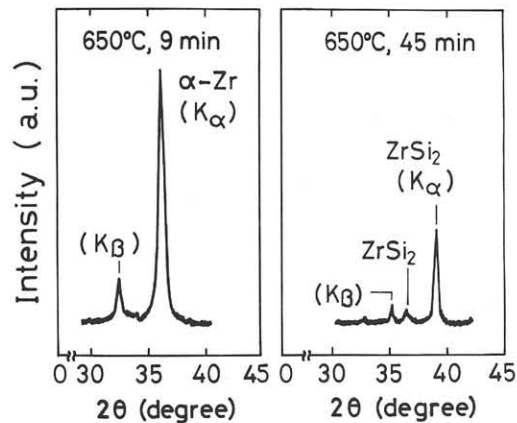


Figure 3 X-ray diffraction spectra from Zr and ZrSi_2 films.

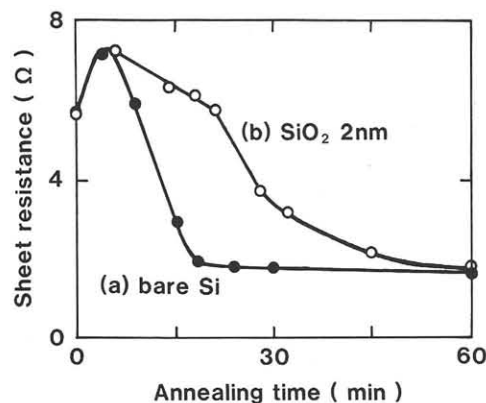


Figure 4 Sheet resistance of Zr/Si systems vs. annealing time.

the Zr-Si interface. Probably, these were introduced into the Zr film at the initial stage of sputtering. During annealing, oxygen diffuses out, and zirconium silicide is formed (Figure 5(b)). Based on these results, it can be understood that hydrogen is effective for the zirconium silicidation (Figure 2) because it reduces zirconium oxide.

To summarize the above results, the process of zirconium silicidation can be described as follows. There is a native silicon oxide film between a silicon substrate and a zirconium film. Also, there is a zirconium oxide layer on the side of the Zr-Si interface in the zirconium film. The zirconium oxide is reduced by hydrogen gas, and oxygen atoms diffuse out. On the other hand, the silicon oxide film is reduced by zirconium, then zirconium oxide formed is reduced as the above description. Successively, silicon and zirconium remained by these reductions react each other to form zirconium silicide.

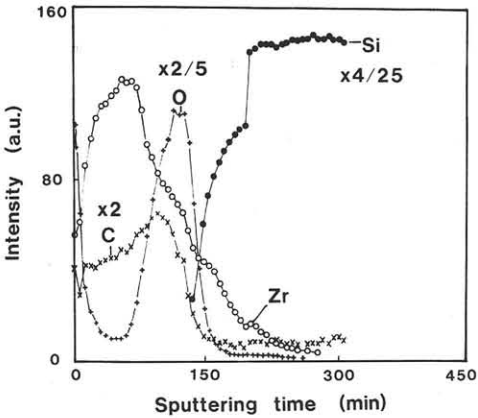
(3) Lateral over-growth of ZrSi_2 and TiSi_2

Samples were prepared by the processes shown in Figure 6. The 10 μm wide lines of SiO_2 were formed on a silicon substrate. The Zr film was deposited on it. The sample was annealed at 670°C in 5% H_2 -Ar ambients for 30 min to form ZrSi_2 . The unreacted metal was etched off by a selective etching solution. For comparison, we have done the same experiment using Ti.

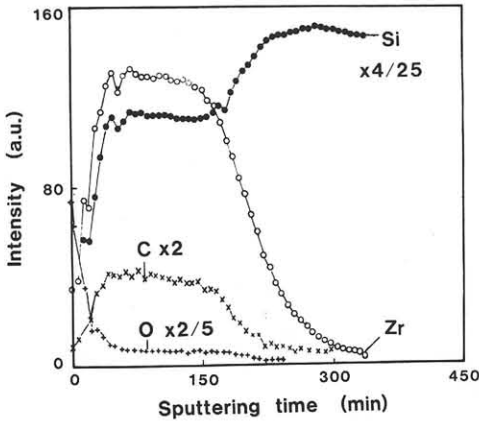
Figure 7(a) and (b) are photomicrographs of the sample surface after etching. It is clear that lateral over-growth of ZrSi_2 is much less than that of TiSi_2 . Also, the boundary between ZrSi_2 and unreacted Zr is very sharp. Furthermore, the surface of the ZrSi_2 film formed on the silicon substrate is smoother than that of the TiSi_2 film.

Figure 8 shows the lateral over-growth length L of ZrSi_2 vs. annealing time. As the graph shows, L is proportional to the square root of the annealing time. Tsukamoto et al. (2) reported that lateral over-growth of TiSi_2 has the same annealing time dependence. These results indicate that silicidation reactions of both Zr and Ti are diffusion limited processes of Si. Therefore, much faster lateral over-growth of TiSi_2 is based on high diffusivity of Si in the TiSi_2 film. Also, fast lateral over-growth of TiSi_2 results in the consumption of a number of Si, especially, around the edge of SiO_2 pattern.

In Figure 7(b), we see that the wider the silicon area (space pattern) is, the more the TiSi_2 grows laterally. However, in Figure 7(a), lateral over-growth length of ZrSi_2 is constant independent of the silicon area.



(a) without annealing



(b) after annealing
annealing : 670°C, 45 min

Figure 5 Depth profiles of Zr/Si systems.

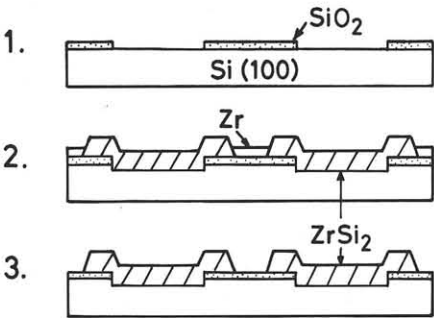
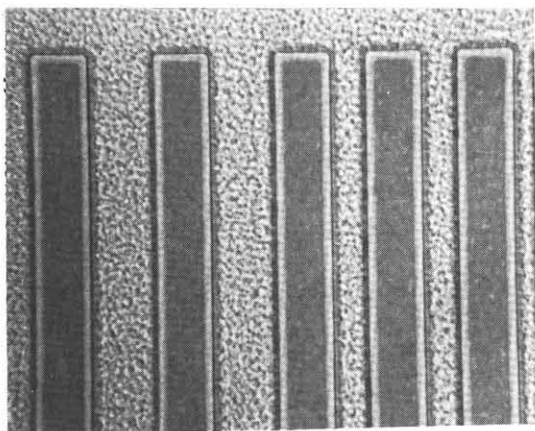
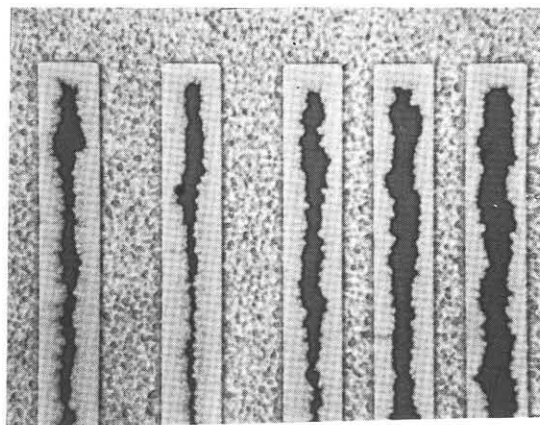


Figure 6 Sample fabrication process.



(a) ZrSi_2



(b) TiSi_2

Figure 7 Photomicrographs of the sample surface.
annealing : 670°C , 30 min

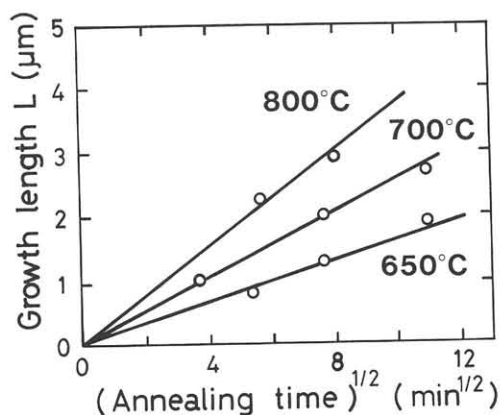


Figure 8 Lateral over-growth length L of ZrSi_2 vs. annealing time.

4. Conclusion

Self-aligned silicidation of Zr was proposed as VLSI fabrication technique which was superior to that of Ti. From investigation of the zirconium silicide formation process, it was found that hydrogen in annealing ambients is effective for the silicidation because zirconium oxide is reduced by H_2 . The oxide film on a silicon surface is also reduced by Zr. Therefore, a zirconium silicide layer can reproducibly be formed even if a thin silicon oxide film exists on a silicon surface after chemical treatment or RIE. Self-aligned silicidation of Zr supplies much less lateral over-growth, smoother surface, and more sharp pattern than that of Ti. This process should be effective for fabricating source/drain and gate regions of MOS transistors.

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