

Diffusion Barrier with Reactively Sputtered TiN Film for Thermally Stable Contact in Advanced VLSI

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The properties of titanium nitride (TiN) film with reactive sputtering and the barrier capability of TiN were investigated with the results that it became clear that oxygen combined with titanium greatly affected the film properties, especially film resistivity. Furthermore, the barrier capability of this TiN film in the structure of W/TiN/Si was determined by both TiN itself and a reaction product which contained Ti, Si, O and N atoms. The ohmic contacts to n^+ and p^+ Si in this structure were maintained even after annealing at 900°C for 6 hours.

1. INTRODUCTION

Thermally stable contact technology is increasingly important for advanced VLSI because of its flexible application to fabrication processes¹). In particular, multilevel interconnection with this technology²) is not restricted by subsequent process temperatures such as reflow of BPSG, densification of interlevel insulations and process temperature at CVD itself. Tungsten (W) and tungsten silicide (WSi_x) are useful for these high temperature processes as an interconnection material. However, W easily reacts with silicon substrate during annealing above 650°C, and WSi_x is not preferable because its resistivity is one level or two higher than that of W is. Therefore, W interconnection requires a diffusion barrier layer between W and Si. For thermally stable contact technologies, W/ WSi_x /Si³), W/TiSi₂/Si⁴), W/TiN/Si⁵) and WSi_x /TiN/TiSi_x/Si⁶) structures have been reported. However, good ohmic properties have still not been obtained for the high temperature process. This can be attributed to the optimization of the TiN film conditions and the interconnection structure.

This paper describes the properties of TiN films which were formed under various conditions with reactive sputtering and their barrier capabilities in the W/TiN/Si structure.

2. EXPERIMENTAL

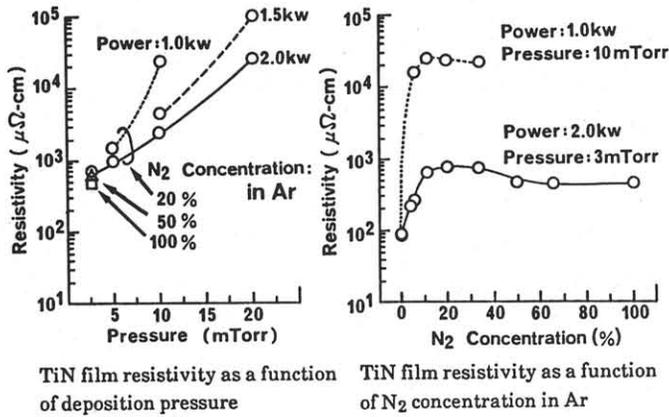
In this experiment, a TiN layer was deposited by DC magnetron sputtering using a

Ti target in N_2 and Ar. The W layer was also deposited by DC magnetron sputtering. The effect of the TiN sputtering condition on the film properties before and after annealing was examined using a four-point probe method, secondary electron microscope (SEM), auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), X-ray diffraction patterns (XD), secondary ion mass spectroscopy (SIMS), and reflection high energy electron diffraction (RHEED). Thermal treatment was performed by furnace annealing after cap SiO_2 deposition. Diffusion barrier properties of TiN were examined in the W/TiN/Si structure by the same methods with regard to the reaction between W and Si. The thickness of TiN and W were 0.08 μ m and 0.3 μ m, respectively. Contact resistance to n^+ and p^+ Si in this structure was measured by the Kelvin method. The n^+ and p^+ diffusion layers were formed by $^{75}As^+$ and $^{11}B^+$ implantations, respectively. Contact sizes were from 0.8 to 4.0 μ m. Annealing temperatures were from 450 to 900°C.

3. RESULTS AND DISCUSSION

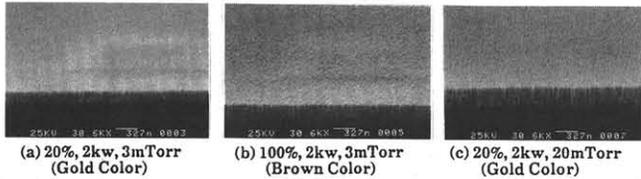
3-1 TiN Film Properties

Fig.1 shows the dependence of the film resistivity on the TiN conditions in the N_2 and Ar. As the power increased and the pressure decreased, the resistivity decreased drastically. This behavior was probably due to impurities in the film. In the low resistivity film deposited at a pressure of 3 mtorr, the film properties greatly depended on N_2 concentration in the Ar, as shown in Fig.2. At 20% N_2 , the film was bright



TiN film resistivity as a function of deposition pressure

TiN film resistivity as a function of N₂ concentration in Ar



SEM photographs of an oblique directional view

Fig. 1 TiN film properties for various conditions of the deposition.

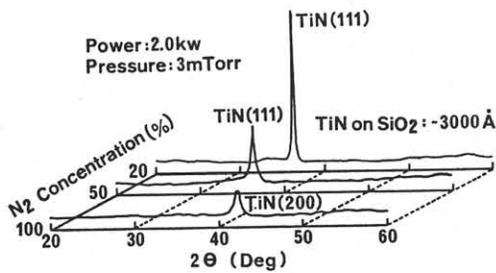


Fig. 2 Changes in X-ray diffraction pattern for low resistive TiN film as a function of N₂ concentration in Ar.

gold in color and strongly oriented toward (111). The plane changed toward (200) at 100%, and a brown film was formed. These films were examined by AES. Fig.3 shows that the high resistivity film contained a large amount of oxygen, and the oxygen peak was also observed in the low resistivity film. The XPS analysis revealed that the oxygen combined with Ti atoms, as shown in Fig.4. It seems that the oxygen absorbed on the surface greatly affected the growth of the film, and for this reason, these films all became columnar polycrystalline structures.

3-2 Barrier Capability of W/TiN/Si structure

Thermal stability of the W/TiN/Si structure was examined. In this structure, TiN films as a diffusion barrier were formed under various conditions. Fig.5 shows the XD spectra

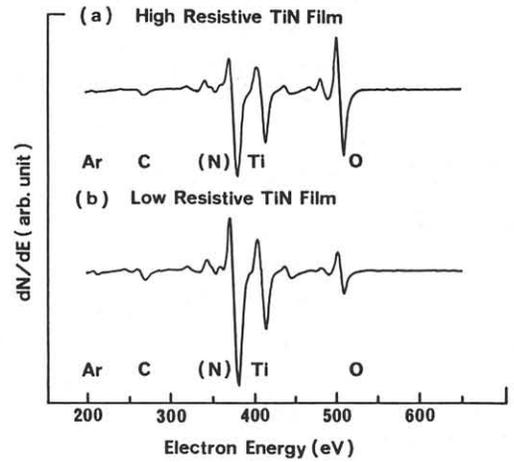


Fig. 3 AES spectra for high and low resistive TiN films.

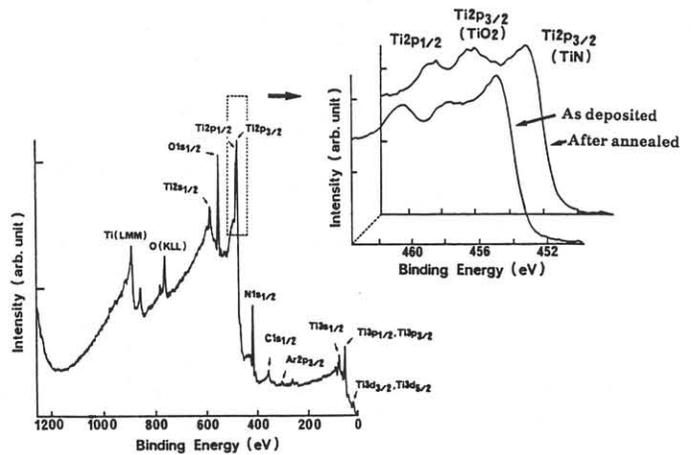


Fig. 4 XPS spectra of TiN films in the case of wide and narrow scanning.

for the W/TiN/Si structure using the low resistivity TiN film before and after annealing at 900°C for 6 hours in N₂. It is apparent that no WSi₂ peaks were observed. In the case of other TiN film, no WSi₂ peaks were observed, either. Next, each atom concentration in respect to depth was examined by SIMS. It is clear that W and Si intermixing was restricted, as shown in Fig.6. However, a bit of the diffusion of Ti and Si was observed. It seems that these atoms only diffused along the grain boundary of columnar W polycrystal, and silicidation did not occur. Therefore, it is considered that the barrier capability in this structure is determined by another factor.

Next, the Si surface was observed after selective removals of W and TiN. Fig.7 shows optical micrographs of the Si surface after removals of W and TiN. In a reference sample of

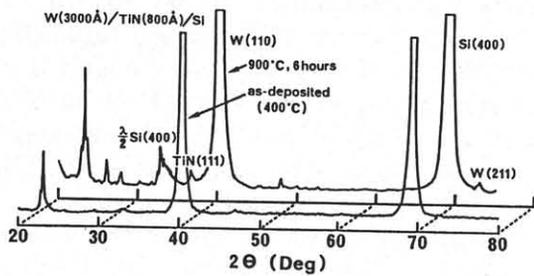


Fig. 5 X-ray diffraction pattern for W/TiN/Si before and after annealing at 900°C for 6 hours.

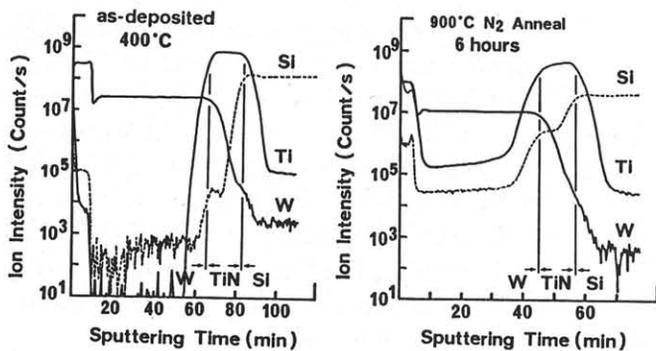


Fig. 6 SIMS depth profiles before and after annealing.

W/Si structure, silicidation occurred and, in another sample structure of W/Ti/Si, strong reaction was observed and WSi_2 was formed through $TiSi_2$. On the other hand, traces of reaction were not observed. However, a newly produced very thin film was formed at the TiN/Si interface. The sheet resistance of this film showed about $2\Omega/\square$, and XPS showed that this newly produced very thin film was a reaction product which contained Ti, Si, O and N atoms, as shown in Fig.8. RHEED pattern from this surface is shown in Fig.9. The pattern indicated that the thin layer was mainly composed of TiO_2 . Taking into account of the sheet resistance, it seems that this layer was a mixture of TiO_2 , Si, and TiN. The TiN barrier capability between W and Si seems to be obtained by TiN itself and this interface layer between TiN and Si.

3-3 Contact Properties

Fig.10 shows the annealing time dependence of contact resistance to n^+ and p^+ Si. It is clear that ohmic contacts to both n^+ and p^+ Si were maintained even after annealing at 900°C for 6 hours. In this process, $^{31}P^+$ or $^{11}B^+$ ion implantation into W was performed to compensate for the loss due to out-diffusion.

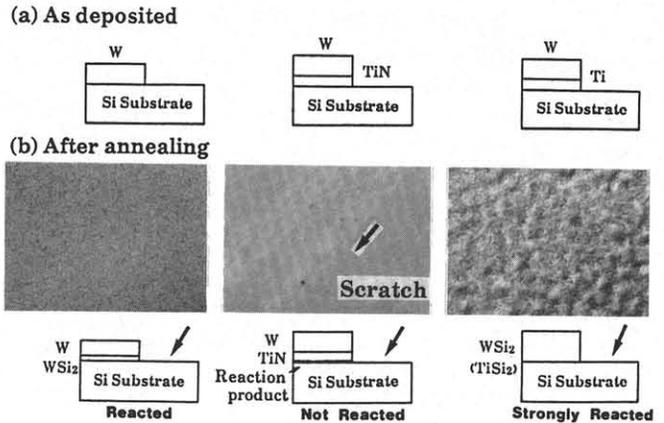


Fig. 7 Optical micrographs of the Si surface after removals of W and TiN.

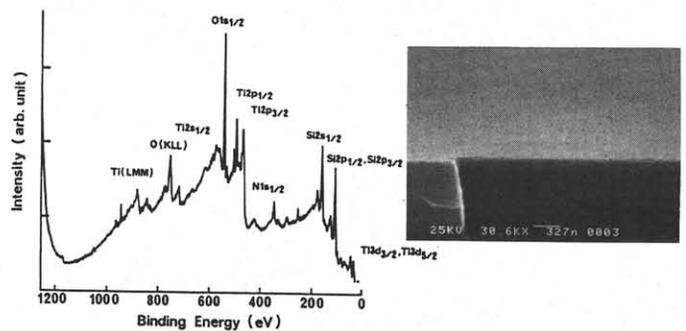


Fig. 8 XPS spectrum and SEM oblique directional view of Si surface after removals of W and TiN.



Fig. 9 RHEED pattern from Si surface after removals of W and TiN.

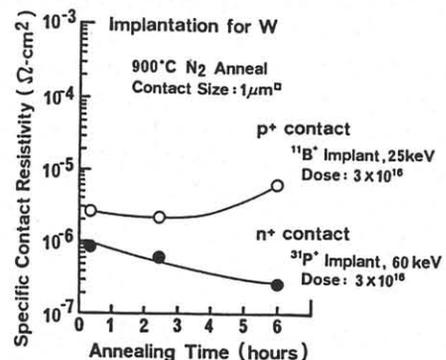


Fig. 10 Contact properties to n^+ and p^+ Si in the W/TiN/Si structure.

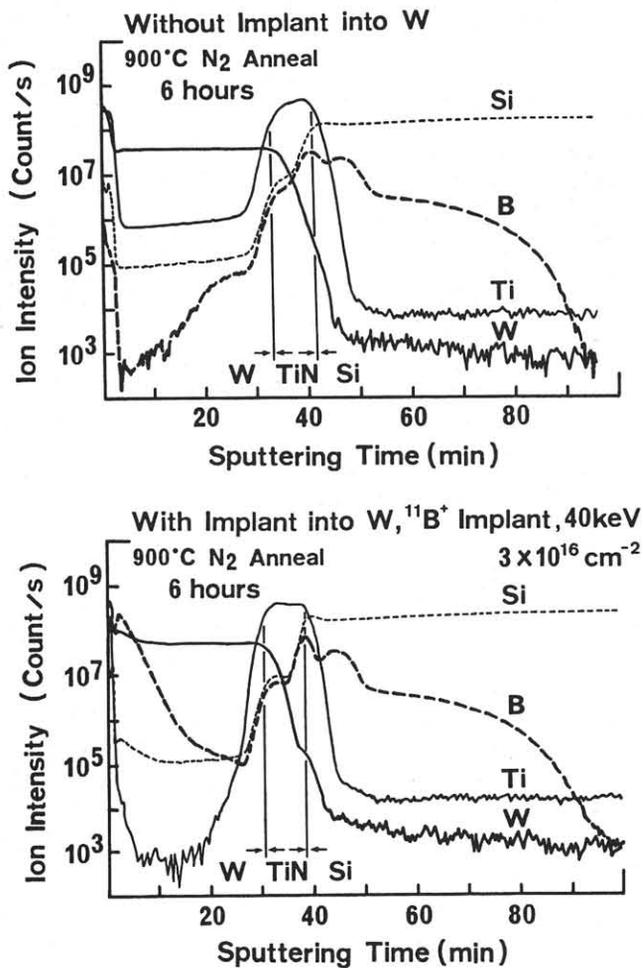


Fig. 11 SIMS depth profiles after annealing.

The contact property to n^+ Si was low enough for high temperature annealing. However, that to p^+ Si has gradually gone up. It seems that ohmic property will be broken down during following annealing. Fig.11 shows SIMS depth profiles of p^+ contact with and without $^{11}\text{B}^+$ ion implantation into W. In the sample without ion implantation, a decrease of surface concentration of boron due to the out-diffusion was observed. However, in the sample with ion implantation, it seems that a decrease of boron concentration at the Si surface was restricted because of the diffusion of boron from the near surface region of W toward the interface. In addition, it seems that the restriction of the diffusion of Ti into W by ion implantation was related with that result.

4.CONCLUSIONS

The properties of reactively sputtered TiN film were investigated and it was clear that the film properties were greatly affected by contained impurities. In particular, TiN film

resistivity was determined by oxygen combined with titanium. These TiN barrier capabilities between W and Si which were formed under various conditions were obtained by both TiN itself and a reaction product which contained Ti, Si, O and N atoms. By using this W/TiN/Si structure, the ohmic contacts to n^+ and p^+ Si were maintained even after annealing at 900°C for 6 hours. This technology will become important for the development of submicron VLSI and future electron devices such as 3-D LSIs.

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