

# Direct Formation of Selective CVD-Al Contact Plug on Titanium Silicide Obtained by Silicidation of Titanium Including Nitrogen

Takayuki KOMIYA, Youichi TAKAI and Hiroshi SHINRIKI

Technology Development Center, LSI Division, Kawasaki Steel Corp.  
1, Kawasaki-cho, Chuo-ku, Chiba 260, Japan

Direct formation of selective CVD-Al contact plug on titanium silicided diffusion region is successfully demonstrated by using titanium silicide including nitrogen ( $TiSi_2(N)$ ) and wet pretreatment before CVD-Al formation.  $TiSi_2(N)$  was formed by silicidation of titanium including nitrogen.  $TiSi_2$  oriented in (040) direction and polycrystalline TiN were observed in the  $TiSi_2(N)$  layer by X-ray diffraction (XRD) analysis. Diffusion of aluminum through the  $TiSi_2(N)$  layer into the Si substrate is assumed to be completely prevented by the TiN microcrystalline in the grain boundary of  $TiSi_2(N)$ . Therefore, our developed CVD-Al contact plug formation processes are very attractive for high performance CMOS using silicide process.

## 1. Introduction

In multilevel interconnection technologies for ULSI, contact / via filling technique using chemical vapor deposition (CVD) becomes essential. Therefore, selective CVD-W and CVD-Al formation on Si substrate have been investigated as promising contact filling processes (1,2). Serious problems of these techniques are thought to be an erosion of Si substrate and selective loss(1). Especially in a case of direct Al-Si contacts, electrical problems like junction leakage and high contact resistance limit its application. On the other hand, selective W or Al growth on silicide, required for high speed CMOS using silicide process, seems to be more possible due to the barrier property of  $TiSi_2$  layer (3). We have reported selective CVD-Al plug formation on a self-aligned nitridation of  $TiSi_2$  layer (4). A direct nitridation of  $TiSi_2$  by rapid thermal annealing in  $NH_3$  ambient was performed to be self-aligned to the contact region, and nitrided  $TiSi_2$  layer provides a diffusion barrier integrity. In addition to diffusion barrier properties, a low resistance and a thermal stability is required for silicide application. Kotaki et al. demonstrated that a sufficient integrity of agglomeration was obtained while keeping low resistance by oxygen free silicidation (OFS) using Ti film sputter-deposited in Ar and  $N_2$  mixed gas atmosphere (5).

This paper describes a direct formation of selective CVD-Al contact plug on a silicide layer obtained by silicidation of sputter-deposited Ti in Ar atmosphere including nitrogen. The behavior of nitrogen in the Ti and the  $TiSi_2$  layer was discussed. The diffusion barrier integrity of the  $TiSi_2$  layer containing nitrogen was evaluated.

## 2. Experimental

Figures 1(a)-1(e) show the key processes for selective CVD-Al contact plug formation on  $TiSi_2$  including nitrogen ( $TiSi_2(N)$ ) layer. The titanium including nitrogen

( $TiN_x$ ,  $x < 1$ ) layer was sputter deposited in mixed gas ambient of Ar and  $N_2$  (a). Content of nitrogen gas during the sputtering was varied from 0 to 3 vol%. Subsequently  $TiSi_2(N)$  was formed on n+/p+ islands by 2-step conventional silicide process (b).

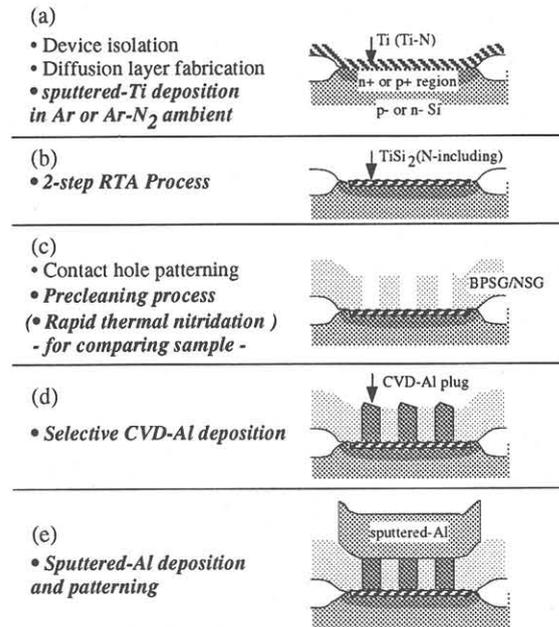


Fig. 1 Sample fabrication processes for selective CVD-Al contact plug formation on N-including  $TiSi_2$  layer

The first step and second step rapid thermal annealings (RTA) were performed at 680 °C for 30 s and at 840 °C for 30 s, respectively. After deposition of inter-dielectric layer, contact holes were dry etched through to the  $TiSi_2$  layer. Diameters of contact holes were varied from 0.4 to 1.0  $\mu m$ . The surface of  $TiSi_2$  layer was pretreated by wet chemicals just before the CVD process (c). Buffered hydrofluoric acid (BHF) and subsequently ammonium peroxide mixture (APM) were used as wet pre-cleaning. For comparison, a sample having  $TiSi_2$  layer with wet pretreatment was

prepared. The  $\text{TiSi}_2$  layer processed by rapid thermal nitridation (RTN) at 865 or 900 °C for 30 s in  $\text{NH}_3$  ambient of 50 Torr was also prepared just before selective CVD-Al plug formation (c). CVD-Al contact plug was formed selectively on the  $\text{TiSi}_2$  layer (d). The deposition condition is as follow. The substrate temperature was varied from 230 to 240 °C. The deposition pressure was kept at 2.0 Torr. Dimethyl Aluminum Hydride (DMAH) was vaporized at room temperature and transported to the CVD reactor with  $\text{H}_2$  gas of 100 sccm. Then the upper Al-Cu layer was sputter deposited and patterned (e). Sintering at 400 °C for 30 min in hydrogen ambient was performed for samples measuring electric properties.

Sheet resistance of the  $\text{TiN}_x$  and the  $\text{TiSi}_2(\text{N})$  film were measured by four-probe method. Phase identification with crystalline nature of the layer was analyzed by X-ray diffraction (XRD). The depth profiles of Ti and N atoms were obtained by X-ray photoelectron spectroscopy (XPS). Filling characteristics and selective loss were observed by scanning electron microscopy (SEM). Leakage current of reverse-biased junction was measured by the n+/p, p+/n junction diode with 2500 contacts of 0.6  $\mu\text{m}$  diameter in the titanium silicided area of 0.04  $\text{mm}^2$ .

### 3. Results and Discussion

Figure 2 shows the change of sheet resistance of as-deposited  $\text{TiN}_x$  film as a function of the nitrogen contents in sputtering ambient. The sheet resistance of  $\text{TiSi}_2(\text{N})$  and  $\text{TiSi}_2$  film after RTA is also shown. The sheet resistance of  $\text{TiSi}_2(\text{N})$  formed by silicidation of  $\text{TiN}_x$  deposited in Ar gas including 1 vol% nitrogen is sufficient low for its silicide application, however, that of  $\text{TiN}_x$  deposited in more than 1 vol% nitrogen atmosphere is remarkably high. Therefore, the  $\text{TiSi}_2(\text{N})$  might be used instead of conventional  $\text{TiSi}_2$ .

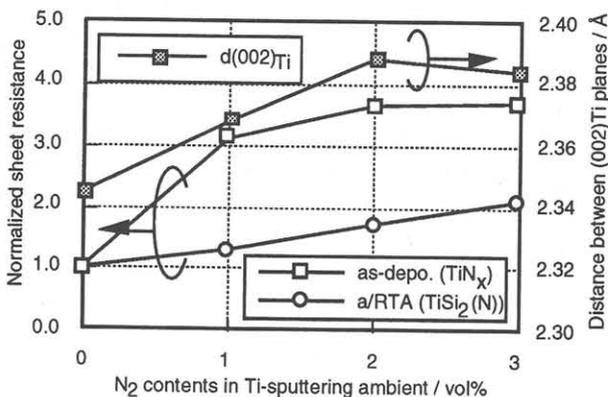


Fig. 2 Normalized sheet resistance of the as-deposited  $\text{TiN}_x$  and after-RTA  $\text{TiSi}_2(\text{N})$  film and distance between (002)Ti planes as a function of  $\text{N}_2$  contents in Ti-sputtering ambient.

XRD spectra (Fig. 3) shows that large (002)Ti peak is observed in  $\text{TiN}_x$  layer sputter deposited in a 1 or 2 vol% nitrogen ambient. Thus, (002)Ti interplanar distance of  $\text{TiN}_x$  became larger than that of Ti layer by an nitrogen

addition (Fig. 2). The distance between (002)Ti planes was 2.344 Å. An interplanar distance of  $\text{TiN}_x$  film deposited in 2 vol% nitrogen ambient was 2.387 Å. These results suggest that the lattice constant of the Ti matrix increased due to the nitrogen atoms and c-axis of Ti crystalline was led vertical to (100)Si plane.

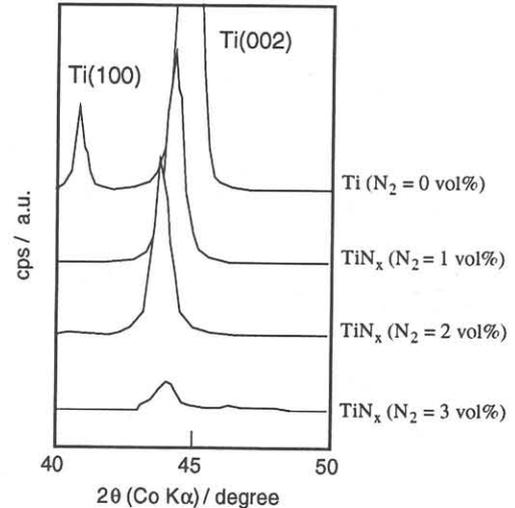


Fig. 3 XRD spectra of the as-deposited Ti and  $\text{TiN}_x$  film

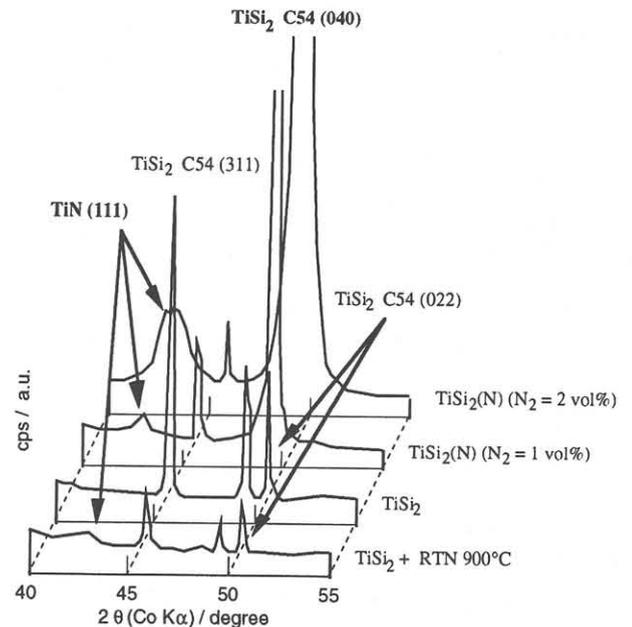


Fig. 4 XRD spectra of the  $\text{TiSi}_2(\text{N})$ ,  $\text{TiSi}_2$  film with and without RTN after second RTA.

Figure 4 shows the XRD spectra of  $\text{TiSi}_2(\text{N})$  and  $\text{TiSi}_2$  films. The (040) orientation of  $\text{TiSi}_2$  and a broad peak of TiN were observed in the spectra of  $\text{TiSi}_2(\text{N})$  layers. These results indicate that the  $\text{TiN}_x$  film oriented in (002)Ti provides the (040) orientation of  $\text{TiSi}_2$  in the  $\text{TiSi}_2(\text{N})$  layer. An amount of TiN peak in  $\text{TiSi}_2(\text{N})$  is larger than that in RTN- $\text{TiSi}_2$ . Figure 5 shows XPS depth profiles for  $\text{TiSi}_2(\text{N})$  layers and  $\text{TiSi}_2$  layers with and without RTN pretreatment. In these profiles, an atomic ratio of nitrogen

in  $\text{TiSi}_2(\text{N})$  layer became higher at deeper side of the layer than both of  $\text{TiSi}_2$  with and without RTN pretreatment. Considering these results, it seems that TiN microcrystalline exists in grain boundary of  $\text{TiSi}_2(\text{N})$ .

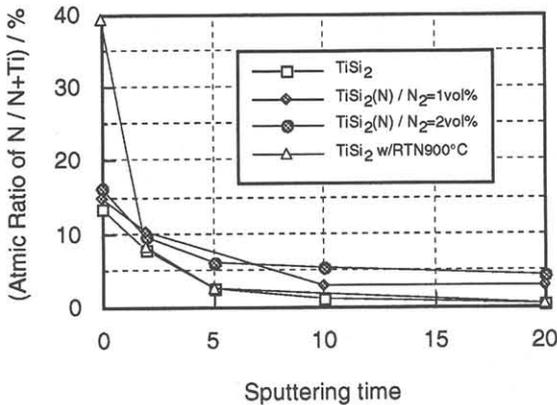


Fig. 5 XPS depth profiles as atomic ratio of  $\text{N}/(\text{N}+\text{Ti})$  from the  $\text{TiSi}_2(\text{N})$  film and the  $\text{TiSi}_2$  film with and without RTN at  $900^\circ\text{C}$  for 30 s.

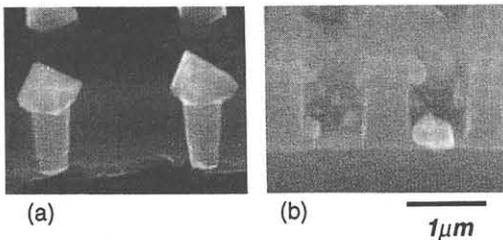


Fig. 6 A cross sectional SEM photograph for fabricated Al contact on the  $\text{TiSi}_2(\text{N})$  layer : (a) with wet pretreatment and (b) without wet pretreatment.

Figure 6(a) shows a cross sectional SEM photographs of CVD-Al contact plugs selectively formed on the  $\text{TiSi}_2(\text{N})$  layer in contact holes of  $0.5\ \mu\text{m}$  diameter. Favorable selective growth from the bottom of contact hole was obtained. In the contrary, formation of contact plugs was not observed without wet treatment as shown in Fig. 6(b). The wet cleaning of the surface of  $\text{TiSi}_2(\text{N})$  at bottom of contact holes before selective CVD is inevitable for a desirable growth of contact plugs on the  $\text{TiSi}_2(\text{N})$ .

Figure 7 shows the leakage current of the reverse biased  $\text{n}+\text{p}$  and  $\text{p}+\text{n}$  junction at 7 V for  $\text{Al}/\text{TiSi}_2/\text{Si}$  and  $\text{Al}/\text{TiSi}_2(\text{N})/\text{Si}$  contact system after sintering. As shown in fig. 7, leakage current in the  $\text{Al}/\text{TiSi}_2(\text{N})/\text{Si}$  contact system, of which  $\text{TiSi}_2(\text{N})$  made from silicidation of  $\text{TiN}_x$  deposited in Ar gas including 1 vol% nitrogen ambient, was sufficiently as low (below  $1\text{E}-11\ \text{A}$ ) as in the  $\text{Al}/\text{RTN}-\text{TiSi}_2/\text{Si}$  system. However, large leakage current was observed in the  $\text{Al}/\text{TiSi}_2/\text{Si}$  contact system without RTN treatment.

Results of physical analyses for  $\text{TiSi}_2(\text{N})$  layer and electrical measurements suggest that a barrier integrity of  $\text{TiSi}_2(\text{N})$  against aluminum diffusion is due to an existence of TiN in the grain boundary of the  $\text{TiSi}_2$ . In addition, it is supposed that a lower concentration of nitrogen at the

surface of the  $\text{TiSi}_2(\text{N})$  layer than the  $\text{RTN}-\text{TiSi}_2$  is advantageous for reducing contact resistance.

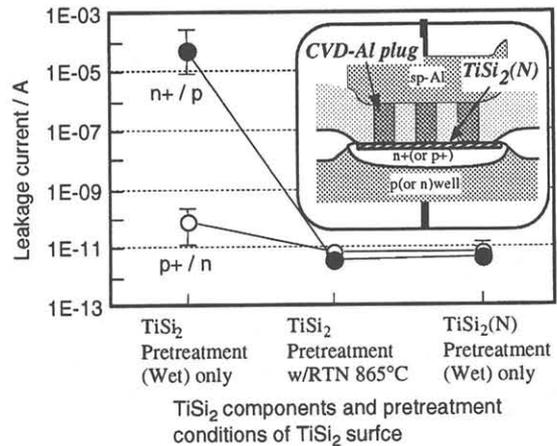


Fig. 7 Reverse-biased junction leakage current at 7 V of  $\text{n}+\text{p}$  and  $\text{p}+\text{n}$  junctions as a function of  $\text{TiSi}_2$  components and pretreatment conditions.

#### 4. Conclusion

Selective CVD-Al contact plug formation directly on titanium silicided diffusion region is successfully demonstrated. The key processes are the  $\text{TiSi}_2(\text{N})$  obtained by silicidation of  $\text{TiN}_x$  deposited in Ar gas including 1 vol% nitrogen and the wet pretreatment before the Al deposition. Highly reliable selective CVD-Al contact plug can be formed on the  $\text{TiSi}_2(\text{N})$  layer, providing an excellent barrier property against aluminum diffusion toward diffused area. At same time, sufficiently low sheet resistance and an integrity of agglomeration are realized by using the  $\text{TiSi}_2(\text{N})$  layer. These results can be explained by formation of microcrystalline TiN in grain boundary of  $\text{TiSi}_2$  layer.

Thus, this process is very promising for CVD-Al contact plug formation of high performance CMOS using salicide process.

#### Acknowledgments

The authors would like to thank stuffs belonging to Process Development Section and Manufacturing Technology Section for help in device fabrication and for their useful technical discussions. We also wish to Dr. Haida for great encouragement.

#### References

- 1) K.Tani et al., Ext. Abs. 1993 Intl. Conf. on SSDM. (1993) 543.
- 2) T. Ohba et al., IEDM Tech. Dig. (1987) 213.
- 3) Martin S. Wang et al., Proc. VLSI Tech. (1991) 41.
- 4) H. Shinriki et al., Ext. Abs. 1994 Intl. Conf. on SSDM. (1994) 946.
- 5) H. Kotaki et al., Ext. Abs. 1994 Intl. Conf. on SSDM. (1994) 628.