論 文
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# 질소분위기에서 순간열처리에 의해 형성시킨 $TiN/TiSi_2$ Contact Barrier Layer의 특성

# Characteristics of $TiN/TiSi_2$ Contact Barrier Layer by Rapid Thermal Anneal in $N_2$ Ambient

李 鐵 眞* · 許 允 宗* · 成 英 權**
**(Cheol-Jin Lee · Yoon-Jong Huh · Yung-Kwon Sung)**

*Abstract* - The physical and electrical properties of $TiN/TiSi_2$ contact barrier were studied. The $TiN/TiSi_2$ system was formed by rapid thermal anneal in $N_2$ ambient after the Ti film was deposited on silicon substrate. The Ti film reacts with $N_2$ gas to make a TiN layer at the surface and reacts with silicon to make a $TiSi_2$ layer at the interface respectively. It was found that the formation of $TiN/TiSi_2$ system depends on RTA temperature. In this experiment, competitive reaction for $TiN/TiSi_2$ system occured above 600℃. Ti-rich $TiN_x$ layer and Ti-rich $TiSi_x$ layer were formed at 600℃. stable structure TiN layer and $TiSi_x$ layer which has $C_{49}$ phase and $C_{54}$ phase were formed at 700℃. Both stable TiN layer and $C_{54}$ phase $TiSi_2$ layer were formed at 800℃. The thickness of $TiN/TiSi_2$ system was increased as the thickness of deposited Ti film increased.

**Key Words** : $TiN/TiSi_2$ system, competitive reaction, TiN and $TiSi_2$ stoichiometry, structure, RTA in $N_2$ ambient

## 1. Introduction

As the density of device increases, the contact size is reduced to submicron. The Al film which contains small amount of Si was used for VLSI

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*正 會 員 : 高麗大 大學院 電氣工學科 博士課程
**正 會 員 : 高麗大 工大 電氣工學科 敎授・工博
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metallization to restrain junction spike at Silicon substrate.[1] But silicon precipitation appeared at the small contact hole when Al-Si film was used for metallization. Si atoms in Al-Si film can migrate easily from line to contact hole and produce silicon nodules at the bottom of contact hole.[2] It results in increasing contact resistance and contact resistance nonuniformity. The barrier metal process was introduced to solve these problems.[3]

In this paper, physical and electrical properties of $TiN/TiSi_2$ system were studied in order to apply that structure as contact barrier layer. The TiN film and the $TiSi_2$ film were formed simultaneously by rapid thermal anneal in $N_2$ ambient.[4, 5] In this case, the Ti film reacts with $N_2$ gas to make a TiN layer at the surface and reacts with Si to make a $TiSi_2$ layer at the interface.[6] it was found that formation of TiN film was limited by a fast diffusion of silicon atom into Ti film to form Tisi film. Properties of $TiN/TiSi_2$ system were investigated at different RTA temperatures. Each films was analyzed by using ESCA, XRD, SEM, TEM, and four point probe resistivity mapping.

## 2. Experimental Method

P-type silicon wafers with (100) orientation and resistivity between 14 and 19 $\Omega$-cm were used in this experiment. Wafers were dipped in 200 : 1HF acid for 90 sec prior to loading in the sputter to remove native oxide on the surface. And then Ti films of 500 Å, 700 Å, 900 Å were deposited by sputter. To obtain $TiN/TiSi_2$ contact barrier layer, deposited Ti films were annealed by RTA at 600℃, 700℃, 800℃, 900℃ in $N_2$ ambient for 30 sec. The sheet resistance was measured by four-point probe, the film structure was analyzed by XRD, the film composition by ESCA, the surface roughness by SEM, and the interface TEM.

## 3. Results and Discussion

High purity Ti film was deposited on the silicon wafer and then $TiN/TiSi_2$ system was formed at the same time by RTA in $N_2$ ambient.

Fig. 1 shows the sheet resistance of $TiN/TiSi_2$ system after rapid thermal anneal in $N_2$ ambient for 30 sec. the sheet resistance was rapidly decreased according to increasing anneal temperature for 500 Å Ti film. But it was saturated above 800℃. This means that reaction is finished and resulting $TiN/TiSi_2$ layer has stable structure at 800℃. From this result, the sheet resistance of $TiN/TiSi_2$ system is shown to be dependant on

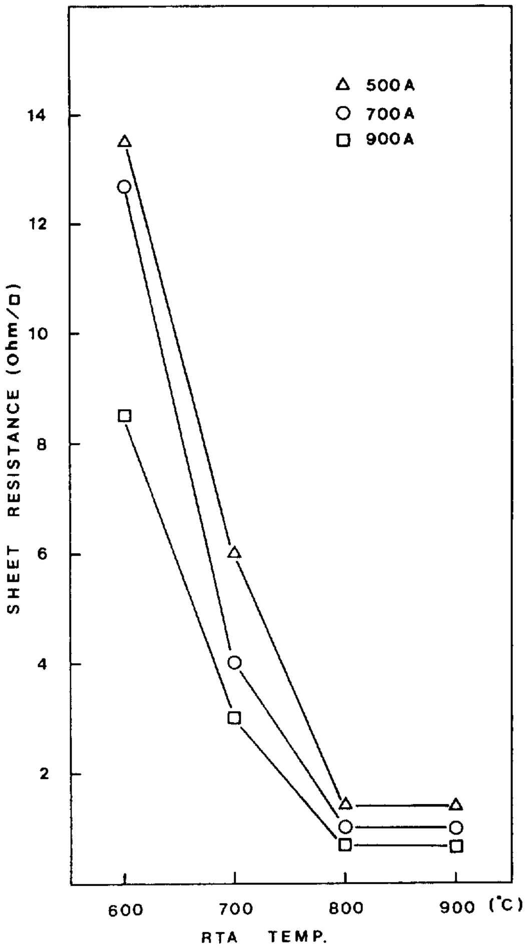
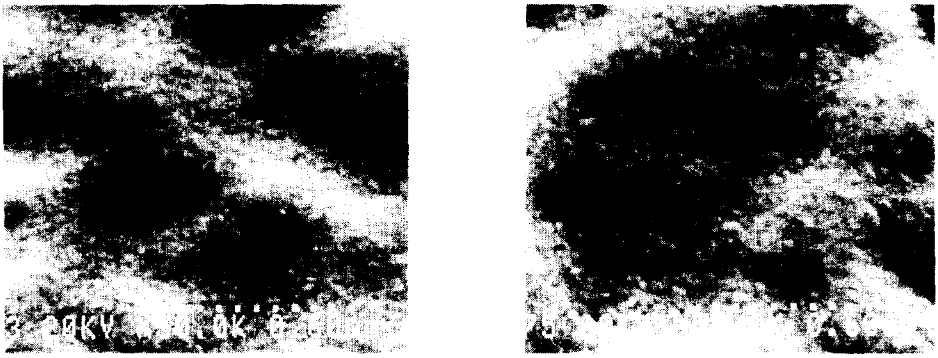
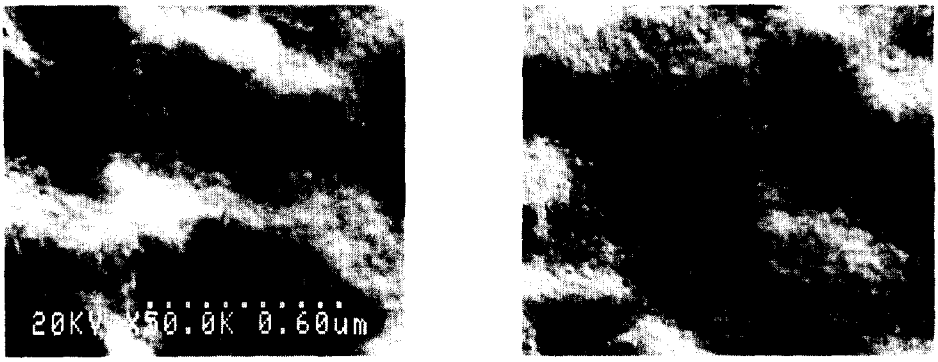


**Fig. 1** Dependance of sheet resistance on the RTA temperature for $TiN/TiSi_2$ system in $N_2$ ambient for 30 sec. Thickness of deposited Ti is 500 Å, 700 Å, 900 Å respectively.



(a) 600℃ Anneal

(b) 700℃ Anneal



(c) 800℃ Anneal

(d) 900℃ Anneal

**Fig. 2** Surface SEM micrograph of $TiN/TiSi_2$ system after RTA in $N_2$ mbient for 30sec. 700 Å Ti film was deposited.

anneal temperature. For 700 Å and 900 Å Ti film, dependacne of sheet resistance on the anneal temperature was similar to the case of 500 Å Ti film. By the way, the sheet resistance of $TiN/TiSi_2$ system decreased as Ti film thickness increased. It was caused by increasing thickness of $TiN/TiSi_2$ system. In Fig. 2, the surface SEM micrograph of $TiN/TiSi_2$ system is shown according to anneal temperature. The surface roughness of $TiN/TiSi_2$ system becomes severe as the anneal temperature increase. This means that reaction is rapidly accelerated according as the anneal temperature increase. But there is no difference about surface roughness between 800℃ and 900℃, because the reaction rate is saturated above 800℃.

Fig. 3 shows ESCA depth profile for $TiN/TiSi_2$ system which was formed at 600℃ in $N_2$ ambient for 30 sec after 700 Å Ti film was deposited on the

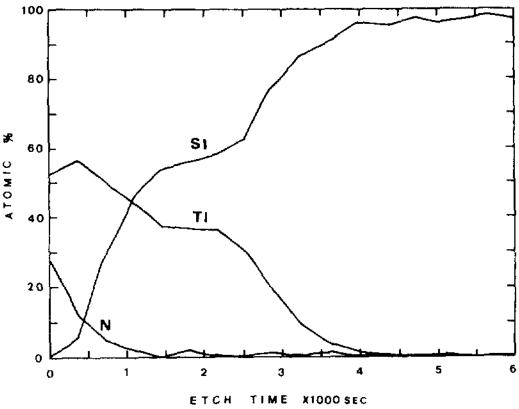


**Fig. 3** ESCA depth profile for $TiN/TiSi_2$ system was formed by RTA at 600℃ in $N_2$ ambient for 30 sec after 700 Å Ti film was deposited.

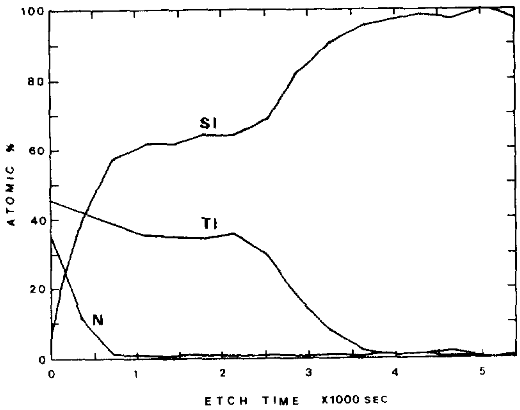


**Fig. 4** ESCA depth profile for TiN/$TiSi_2$ system was formed by RTA at 700℃ in $N_2$ ambient for 30 sec after 700 Å Ti film was deposited.

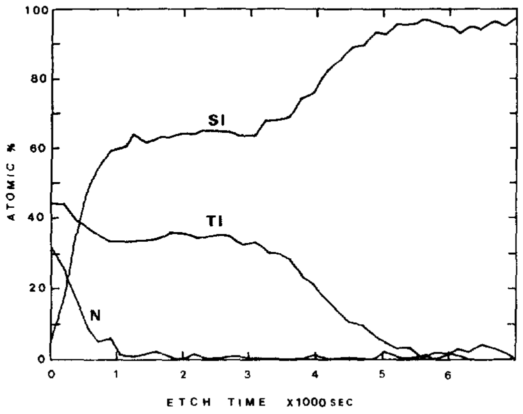


**Fig. 5** ESCA depth profile for TiN/$TiSi_2$ system was formed by RTA at 800℃ in $N_2$ ambient for 30 sec after 700 Å Ti film was deposited.

silicon substrate. It shows that Ti-rich $TiSi_x$ film was formed at the interface and Ti-rich $TiN_x$ film was formed at the surface because the anneal temperature was not sufficient to silicidation and nitridation respectively. It also shows that thick $TiN_x$ layer was formed at the surface. From this result, we can assert that competitive reaction of TiN/$TiSi_2$ system occurs at 600℃

Fig. 4 shows ESCA depth profile for TiN/$TiSi_2$ system which was formed at 700℃. It looks like that Ti-rich $TiSi_2$ film was formed at the interface but stable stoichiometric TiN film was formed at the surface. The thickness of $TiSi_2$ film was increased while TiN film was decreased. It reveals that silicidation is more active than nitridation at 700℃.

Fig. 5 shows ESCA depth profile for TiN/$TiSi_2$ system which was formed at 800℃. It shows both $TiSi_2$ film and TiN film has stable composition. Thick $TiSi_2$ layer was formed at the interface while thin TiN layer was formed at the surface. This means the silicidation reaction was rapidly accelerated as anneal temperature increased.[7] Sun et al. announced that the silicidation reaction is faster as the reaction tem perature is higher, on the contrary the nitridation reaction is faster as the reaction temperature is lower.[8]

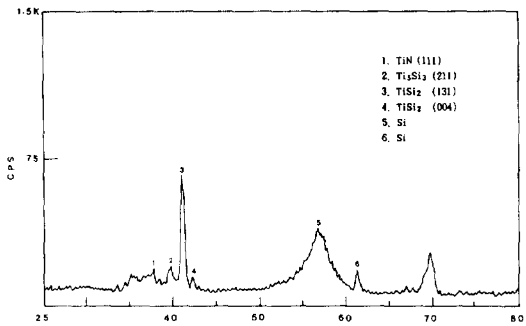


**Fig. 6** X-ray diffraction peak for TiN/$TiSi_2$ system was formed by RTA at 600℃ in $N_2$ ambient for 30sec.

Fig. 6 shows X-ray diffraction peak for TiN/$TiSi_2$ system which was formed in $N_2$ ambient for 30 sec at 600℃. The peak 1 represents TiN(111) and the peak 2, 3, 4 and 5 represent $Ti_5Si_3$(211), $TiSi_2$(131), $TiSi_2$(040) and Si respectively. By the way, the struture of $TiSi_2$(131) is $C_{49}$ phase and $TiSi_2$(040) is $C_{54}$ phase. Peaks are small and profiles are not clear for peak 1 and peak 2 in this figure. It means that TiN is Ti-rich $TiN_x$ film and $TiSi_2$ has un stable strueture

Fig. 7 shows X-ray diffraction peak for TiN/$TiSi_2$ system which was formed at 700℃. In this figure, peak 1 represents TiN(111) and peak 2, 3, 4, 5 and 6 represent $TiSi_2$(311), $TiSi_2$(131), $TiSi_2$ (004), $TiSi_2$(022) and $TiSi_2$(313) respectively. It

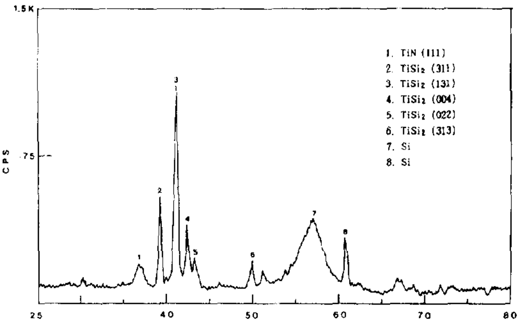


**Fig. 7** X-ray diffraction peak for TiN/TiSi$_2$ system was formed by RTA at 700℃ in N$_2$ ambient for 30sec.

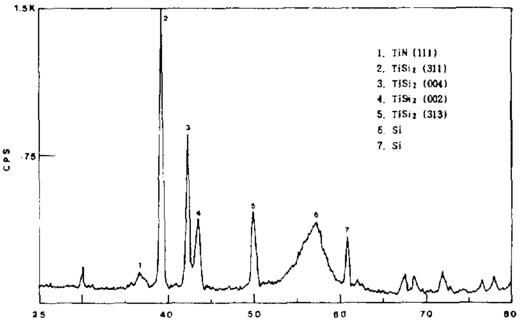


**Fig. 8** X-ray diffraction peak for TiN/TiSi$_2$ system was formed by RTA at 800℃ in N$_2$ ambient for 30 sec.

was known TiSi$_2$(131) has C$_{49}$ phase but another TiSi$_2$ have C$_{54}$ phase. From these results, we know that TiN film has stable structure but TiSi$_2$ film has unstable C$_{49}$ phase and stable C$_{54}$ phase at the same time.

Fig. 8 shows X-ray diffraction peak for TiN/TiSi$_2$ system which was formed at 800℃. The peak 1 represents TiN(111) and peak 2, 3, 4 and 5 represent all C$_{54}$ phase TiSi$_2$, moreover all peaks are clear. Therefore both TiN and TiSi$_2$ have stable structure film.[9] According to XRD analysis, the phase of TiSi$_2$ was changed from C$_{49}$ TiSi$_2$ to C$_{54}$ TiSi$_2$ as anneal temperature increased.

Fig. 9 shows cross-sectional TEM micrograph of TiN/TiSi$_2$ system at 700℃ in N$_2$ ambient for 30sec for 500 Å Ti film. This figure shows that thick TiSi$_2$ layer was formed at the interface while thin TiN layer was formed at the surface. It reveals

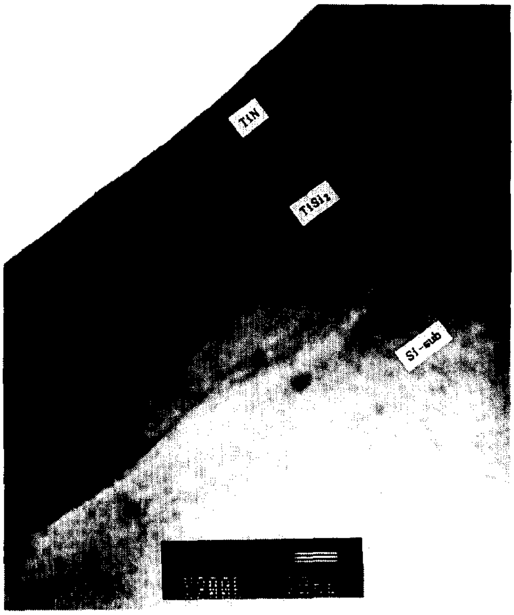


**Fig. 9** Cross-sectional TEM micrograph for TiN/TiSi$_2$ system after RTA at 700℃ in N$_2$ ambient for 30 sec. Thickness of deposited Ti was 500 Å.

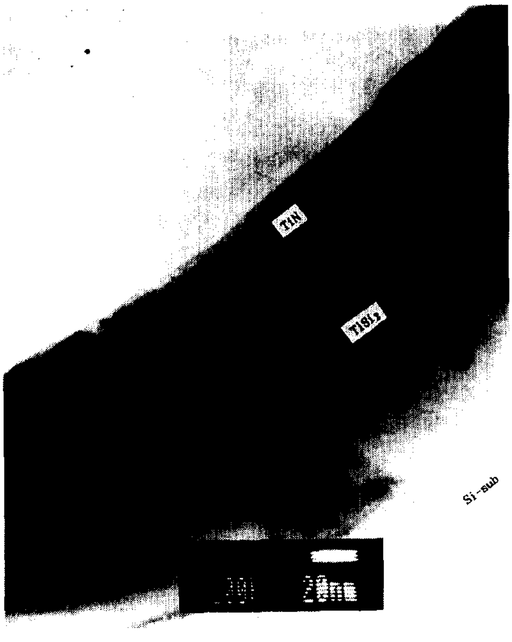


**Fig. 10** Cross-sectional TEM micrograph for TiN/TiSi$_2$ system after RTA at 700℃ in N$_2$ ambient for 30 sec. Thickness of deposited Ti was 700 Å

that silicidation reaction is rapidly advanced at 700℃ annel. The thickness of TiN film was 220 Å and that of $TiSi_2$ film was 780 Å

Fig. 10 shows cross-sectional TEM micrograph of TiN/$TiSi_2$ system for 700 Å Ti film. This figure shows that 1080 Å $TiSi_2$ layer was formed at the interface but 270 Å TiN layer was formed at the surface. From this result, we can conclude that silicidation reaction is more promotive to nitridation reaction when anneal temperature is higher than 700℃

## 4. Conclusion

It was possible to make TiN/$TiSi_2$ contact barrier layer simultaneously by RTA in $N_2$ ambient. The formation of TiN layer was supposed to be limited by the silicide formation and the structure of resulting TiN/$TiSi_2$ system was dependant on RTA temperature.

At 600℃, Ti-rich $TiN_x$ film was formed at the surface and $Ti_5Si_3$ film was formed at the interface.

At 700℃, TiN film which has stable structure and stoichiometry was formed at the surface but $TiSi_2$ film which was formed at the interface represented $C_{49}$ phase and $C_{54}$ phase.

At 800℃, TiN film which has stable structure and stoichiometry was formed at the surface and $C_{54}$ phase $TiSi_2$ film was formed at the interface.

The phase of $TiSi_2$ film was changed from $C_{49}$ phase to $C_{54}$ phase as anneal temperature increased.

As the anneal temperature increased, the thickness of $TiSi_2$ layer was increased while TiN layer was decreased.

The thickness of TiN/$TiSi_2$ system was increased as the thickness of deposited Ti film increased.

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