論 文
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NH_3 분위기에서 급속열처리에 의한 $TiN/TiSi_2$이중구조막의 특성에 대한 고찰

A Study on the Properties of $TiN/TiSi_2$ Bilayer by a Rapid Thermal Anneal in NH_3 Ambient

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Abstract - The physical and electrical properties of $TiN/TiSi_2$ bilayer were studied. The $TiN/TiSi_2$ bilayer was formed by rapid thermal anneal in NH_3 ambient after the Ti film was deposited on silicon substrate. The Ti film reacts with NH_3 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 $TiN/TiSi_2$ bilayer depends on RTA temperature. In this experiment, competitive reaction for $TiN/TiSi_2$ bilayer occured above 600 ℃. Ti-rich TiN_x layer and Ti-rich $TiSi_x$ layer were formed at 600 ℃. stable structure TiN layer $TiSi_2$ 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 $TiN/TiSi_2$ bilayer was increased as the thickness of deposited Ti film increased.

Key Words : $TiN/TiSi_2$ bilayer, RTA in NH_3 ambient, $TiN/TiSi_2$ Competitive reaction, $TiN/TiSi_2$ composition, $TiN/TiSi_2$ structure

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1. Introduction

The Al film which contains small amount of Si was used for VLSI metallization to restrain junction spike at Si substrate.[1] But Si atoms in Al-Si film can migrate easily from line to contact hole

and produce silicon nodules at the small contact hole.[2] It results in increasing contact resistance and contact resistance nonuniformity. The TiN/$TiSi_2$ barrier metal process was introduced to solve these problems.[3]

We already reported to the properties of TiN/$TiSi_2$ bilayer by RTA in N_2 ambient[4].

But TiN/$TiSi_2$ bilayer by RTA in N_2 ambient was not acceptible level for contact barrier layer because it is difficult to obtain thick layer and good barrier property of TiN.

In this paper, the properties of TiN/$TiSi_2$ bilayer was investigated in order to improve the contact barrier property. Both the TiN film and the $TiSi_2$ film was formed simultaneously by rapid thermal anneal in NH_3 ambient.[5, 6]

2. Experimental Method

P-type silicon wafers with (100) orientation and resistivity between 14 and 19 Ω-cm were used in this experiment. The wafers were cleaned by using RCA cleanning procedure and 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 50nm, 70nm, 90nm were deposited by sputter. To make a TiN/$TiSi_2$ bilayer, deposited Ti films were annealed by RTA at 600℃, 700℃, 800℃, 900℃ in NH_3 ambient for 30sec. The sheet resistance was measured by four-point probe, the film structure was analyzed by XRD, the film composition by ESCA, and the interface of TiN/$TiSi_2$ bilayer by TEM.

3. Results and Discussion

The Ti film was deposited on Si substrate by DC sputtering method. And then the Ti film reacts with NH_3 gas to make a TiN layer at the surface and reacts with Si to make a $TiSi_2$ layer at the interface.[7]

Figure 1 shows the sheet resistance of TiN/$TiSi_2$ bilayer for 50nm, 70nm, 90nm Ti film, respectively. The sheet resistance rapidly decreases as anneal temperature is increased, but it remained constant above 800℃. This means that reaction is finished and resulting TiN/$TiSi_2$ bilayer has stable structure at 800℃.

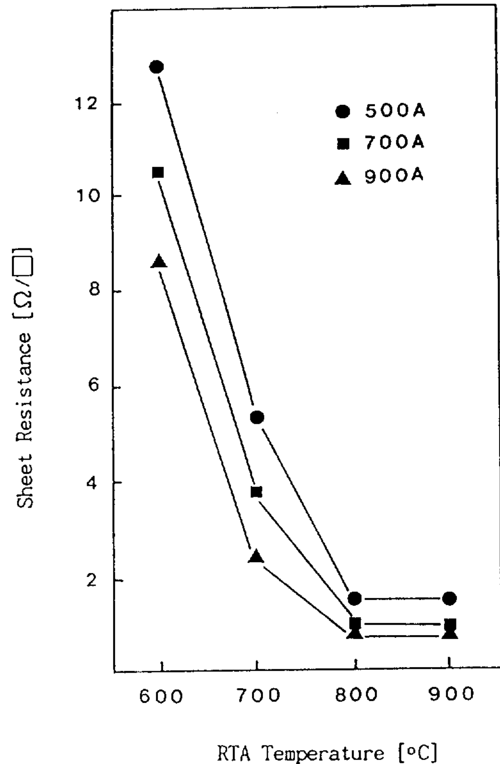

Fig. 1 Dependance of sheet resistance on the RTA temperature for TiN/$TiSi_2$ bilayer in NH_3 ambient for 30sec. Thickness of deposited Ti is 50nm, 70nm, 90nm, respectively.

The sheet resistance of TiN/$TiSi_2$ bilayer decreases as Ti film thickness is increased because the thickness of TiN/$TiSi_2$ bilayer increases.

To confirm the composition of TiN/$TiSi_2$ bilayer, ESCA depth profile was investigated.

Figure 2 indicates ESCA depth profile for TiN/$TiSi_2$ bilayer which was formed at 600℃ in NH_3 ambient for 30 sec after 70nm Ti film was deposited on silicon substrate. Ti-rich $TiSi_x$ film is formed at the interface and Ti-rich TiN_x film is formed at the surface, because the anneal temperature is not sufficient to silicidation and nitridation respectively. It also reveals that thick TiN_x layer is formed at the surface. This result suggests that competitive reaction of TiN/$TiSi_2$ bilayer occurs at 600℃.

ESCA depth profile for TiN/$TiSi_2$ bilayer which was formed at 700℃ is shown in Fig. 3. Ti-rich

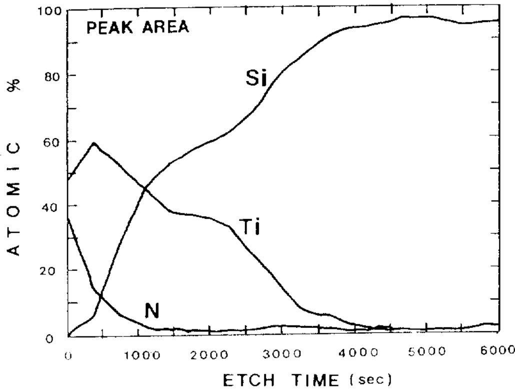

Fig. 2 ESCA depth profile for $TiN/TiSi_2$ bilayer formed by RTA at 600℃ in NH_3 ambient for 30sec.

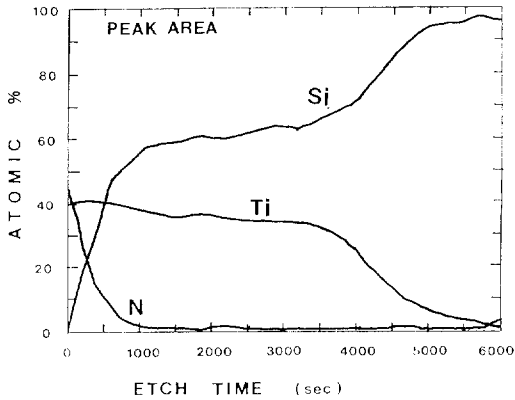

Fig. 3 ESCA depth profile for $TiN/TiSi_2$ bilayer formed by RTA at 700℃ in NH_3 ambient for 30sec.

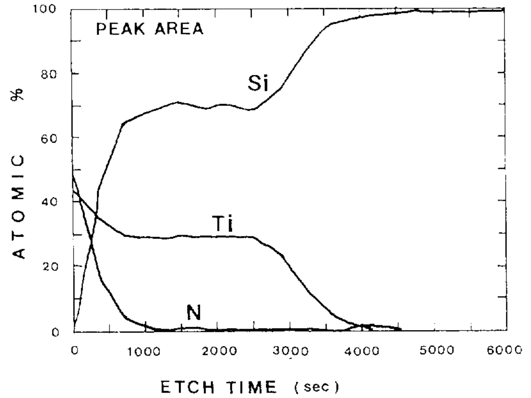

Fig. 4 ESCA depth profile for $TiN/TiSi_2$ bilayer formed by RTA at 800℃ in NH_3 ambient for 30sec.

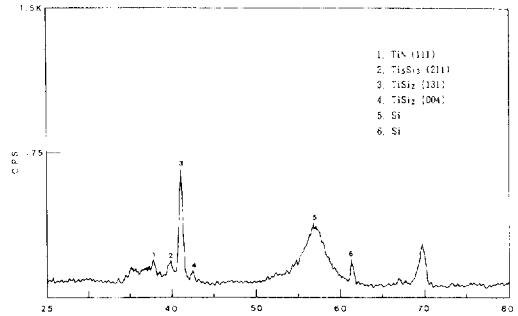

Fig. 5 X-ray diffraction peak for $TiN/TiSi_2$ bilayer formed by RTA at 600℃ in NH_3 ambient for 30 sec.

$TiSi_x$ film is formed at the interface while stable stoichiometric TiN film is formed at the surface. At 700℃, the thickness of $TiSi_x$ film increases but that of TiN film decreases. It reveals that silicidation is more actively advanced in comparison with nitridation.

Figure 4 shows ESCA depth profile for $TiN/TiSi_2$ bilayer which was formed at 800℃. Both $TiSi_2$ film and TiN film has stable composition. It is clear that thick $TiSi_2$ layer is formed at the interface while thin TiN layer is formed at the surface, because silicidation reaction rapidly accelerates with increasing anneal temperature. [8] According to Okamoto et al., the silicidation reaction is faster as the reaction temperature is higher, on the contrary the nitridation reaction is faster as the reaction temperature is lower.[9]

X-ray diffraction was carried out to determine the crystalline structure of the $TiN/TiSi_2$ bilayer. Figure 5 shows X-ray diffraction peak for $TiN/TiSi_2$ bilayer which was formed in NH_3 ambient for 30 sec at 600℃ anneal. The peak 1 represents TiN(111), and the peak 2, 3, 4, and 5 represent Ti_5Si_3(211), $TiSi_2$(131), $TiSi_2$(004), and Si, respectively. In this figure, $TiSi_2$(131) is unstable C_{49} phase and $TiSi_2$(004) is stable C_{54} phase moreover peaks are small and obscure. This result

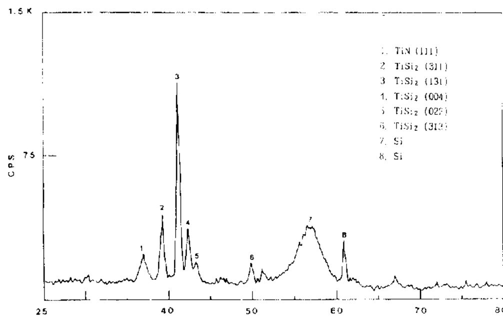

Fig. 6 X-ray diffraction peak for TiN/$TiSi_2$ bilayer formed by RTA at 700℃ in NH_3 ambient for 30sec.

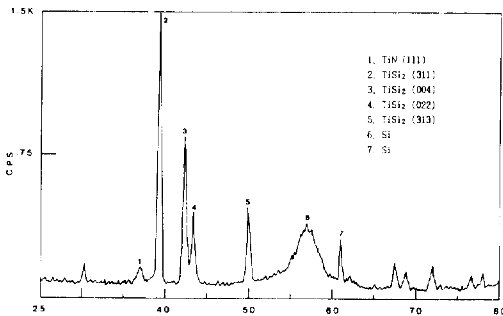

Fig. 7 X-ray diffraction peak for TiN/$TiSi_2$ bilayer formed by RTA at 800℃ in NH_3 ambient for 30sec.

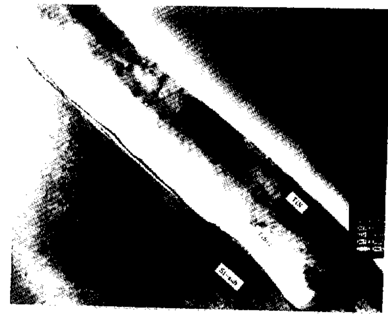

Fig. 8 Cross-sectional TEM micrograph of TiN/$TiSi_2$ bilayer by RTA at 600℃ in NH_3 ambient for 30sec for 50nm Ti film.(x200 k)

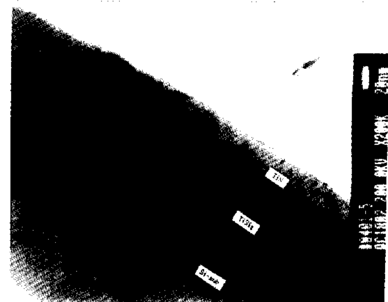

Fig. 9 Cross-sectional TEM micrograph of TiN/$TiSi_2$ bilayer by RTA at 600℃ in NH_3 ambient for 30sec for 70nm Ti film.(x200 k)

indicates that TiN is Ti-rich TiN_x and $TiSi_2$ contains Ti_5Si_3 and C_{49} phase. $TiSi_2$.

Figure 6 demonstrates X-ray diffraction peak for TiN/$TiSi_2$ bilayer 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.

$TiSi_2$(131) points to unstable C_{49} phase but the others point to stable C_{54} phase. Therefore TiN film has stable stoichiometry but $TiSi_2$ film has C_{49} phase and C_{54} phase.

X-ray diffraction peak for TiN/$TiSi_2$ bilayer which was formed at 800 is shown in Fig. 7. Peak 1 is TiN(111), and peak 2, 3, 4, and 5 represent all C_{54} phase $TiSi_2$, moreover all peaks are clear. Therefore both TiN film and $TiSi_2$ film has stable structure.[10] In addition, It is apparent that the phase of $TiSi_2$ film changes from C_{49} phase $TiSi_2$ to C_{54} phase $TiSi_2$ as anneal temperature is increased.

Figure 8 shows cross-sectional TEM micrograph of TiN/$TiSi_2$ bilayer which was formed at 600℃ in NH_3 ambient for 30 sec after 50nm Ti film was deposited. In this figure, 40nm TiN film is shown at the surface and 58nm $TiSi_2$ film is shown at the interface.

This result represents that competitive reaction of TiN/$TiSi_2$ bilayer occures at 600℃ and thick TiN is obtained because nitridation is more active at low temperature. Cross-sectional TEM micrograph of TiN/$TiSi_2$ bilayer at 600℃ for 70nm Ti film is shown in Fig. 9. Reaction is similar to the case of 50nm Ti film, but total thickness of TiN/$TiSi_2$ bilayer is increased. In this case, the thick-

Fig. 10 Cross-sectional TEM micrograph of $TiN/TiSi_2$ bilayer by RTA at 700℃ in NH_3 ambient for 30sec for 50nm Ti film. (x200k)

Fig. 11 Cross-sectional TEM micrograph of $TiN/TiSi_2$ bilayer by RTA at 700℃ in NH_3 ambient for 30sec for 70nm Ti film. (x150 k)

ness of TiN film was 42nm and that of $TiSi_2$ film was 74nm.

Figure 10 indicates cross-sectional TEM micrograph of $TiN/TiSi_2$ bilayer at 700℃ after 50nm Ti film. In this case, thickness of $TiSi_2$ layer increases at the interface while TiN layer decreases at the surface. It reveals that silicidation reaction is rapidly advanced with increasing temperature. The thickness of TiN film was 25nm and that of $TiSi_2$ film was 70nm.

Figure 11 shows cross-sectional TEM micrograph of $TiN/TiSi_2$ bilayer at 700℃ in after 70nm Ti film. This figure shows that 110nm $TiSi_2$ layer is formed at the interface, on the contrary, 34nm TiN layer is formed at the surface. These results indicate that silicidation reaction is more promotive to nitridation reaction when anneal temperature is higher than 700℃.

4. Conclusion

It has been found that both TiN layer and $TiSi_2$ layer is formed simultaneously by RTA in NH_3 ambient. It is possible to obtain thick TiN layer at low temperature anneal in NH_3 ambient, and the thickness of TiN layer is limited by the silicide formation. The structure of resulting $TiN/TiSi_2$ bilayer is dependant on RTA temperature.

At 600℃, Ti-rich TiN_x layer is formed at the surface, but $TiSi_2$ layer represents Ti_5Si_3 and C_{49} $TiSi_2$ at the interface.

At 700℃, TiN layer has stable structure and stoichiometry but $TiSi_2$ layer reveals both C_{49} $TiSi_2$ and C_{54} $TiSi_2$.

At 800℃, TiN and $TiSi_2$ layer represent stable structure and atomic composition of these layer represents also stable stoichoimetry.

The structure of $TiSi_2$ film changes from C_{49} phase $TiSi_2$ to C_{54} phase $TiSi_2$ as anneal temperature is increased.

The thickness of $TiSi_2$ layer increases while TiN layer decreases as the anneal temperature is increased.

The thickness of $TiN/TiSi_2$ bilayer increases as the thickness of deposited Ti film is increased.

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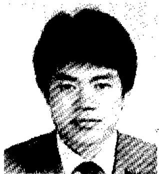

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