An Environment-Insensitive Trilayer Structure for Titanium Silicide Formation

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ABSTRACT

A Si/Mo/Ti trilayer structure which consists of a top, insulating Si film, a middle buffering Mo film, and a bottom Ti film is proposed for $TiSi_2$ formation on n^+ polysilicon. Since residual oxidants and impurity gases are effectively blocked by the Si layer, an N_2-flowing open tube with stringent environmental control is enough for the formation process above 750°C. The resultant sheet resistance of the silicided polysilicon is as low as 2% with good uniformity. Moreover, the resultant SiO_2 thickness loss is reduced, and no metallic luster is shown on the oxide surface, even after the anneal at 800°C. The lateral formation of $TiSi_2$ is found to be greatly suppressed in the anneal at 750°C for 15 min. Low resistivity, high environmental insensitivity, small oxide loss, and less lateral growth make the $TiSi_2$ formation using the trilayer structure an attractive and promising method in many IC applications using silicides.

It is known that titanium silicide ($TiSi_2$) is one of the promising gate and interconnect materials for future integrated circuits. Generally $TiSi_2$ can be thermally formed by reacting thin titanium films with polycrystalline silicon (1) or by sintering codeposited films on polysilicon or SiO_2 (2). However, due to high oxidation rate of Ti to some oxidants, the quality of the resultant $TiSi_2$ is very sensitive to oxidizing gases in the annealing or sintering ambient. Therefore, a very stringent control on the ambient, especially the control of the residual oxygen, is required. This often increases process cost and causes difficulties in yield improvement. Recently, a Mo/Ti bilayer structure has been proposed (3) to solve this problem. However, because oxidants may penetrate the top Mo layer and react with the bottom Ti layer, it still requires some degree of ambient control.

In this study, a Si/Mo/Ti trilayer structure is proposed for $TiSi_2$ formation. Experimental results have shown that a good-quality $TiSi_2$ layer can be formed on n^+ polysilicon in a conventional N_2-flowing ambient. Thus, no stringently controlled ambient is required in the annealing or sintering process. Moreover, the undesired reaction between Ti and SiO_2 (4) can be weakened which results in a smaller SiO_2 thickness loss. As to the lateral formation problem, the trilayer structure annealed at 750°C for a shorter time (15 min) has much less lateral formation of $TiSi_2$. It is possible, therefore, to find an optimal annealing condition in which the oxide loss, the lateral formation, and the resistivity of $TiSi_2$ reach a satisfactory compromise for IC applications.

Experimental

The (100) p-type starting wafers with resistivity of 20-55 Ω/□ were first oxidized to form a 500 nm SiO_2 layer. A polysilicon layer of 500 nm was then deposited by using LPCVD and doped by using $POCl_3$ diffusion. The measured sheet resistance of the resulting n^+ polysilicon film was 50-55 Ω/□. The polysilicon layer was then patterned into long strip lines which can be employed to measure the sheet resistance after silicidation.

The wafers were then put into the vacuum chamber of a dual-E-gun multiple-crucible evaporator. A trilayer structure which consists of 50 nm Ti, 100 nm Mo, and 100 nm Si films successively deposited by using different crucibles in the same vacuum, was formed. The film thickness was controlled by a thickness monitor in the chamber. The cross-sectional view of the trilayer structure is shown in Fig. 1. Then the conventional two-step silicide formation process (3) was applied. In the first step called the sintering or the first annealing step, the wafers were sintered at five different temperatures (600°, 650°, 700°, 750°, and 800°C) for 30 or 60 min in an N_2-flowing open tube. After the first anneal, the top Si layer was removed by plasma etching, whereas the Mo layer and the unreacted Ti layer were etched in a solution of NH_4OH:H_2O_2:H_2O = 1:1:2 for 10-20 min. Then the sheet resistance of the polysilicon strip line was measured. Following was the second annealing process at 800°C in an N_2-flowing open tube for 30 min. After the second anneal, the sheet resistance was measured again. Besides the resistivity measurement, the AES analyses were performed on both the as-deposited and the annealed samples to investigate their physical properties.

In the $TiSi_2$ formation process, the interaction between Ti and SiO_2 is a major concern (4), especially in self-aligned silicide technology (5). Another group of wafers was used to investigate this interaction. These wafers went through the same process cited above. The oxide thickness and the index of refraction before and after the silicide formation were measured by an ellipsometer. Selected samples were also analyzed by AES.

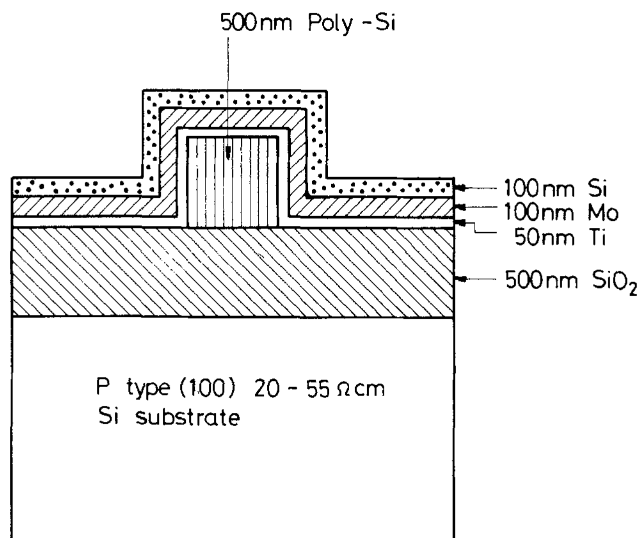

Fig. 1. Cross-sectional view of a Si/Mo/Ti trilayer structure

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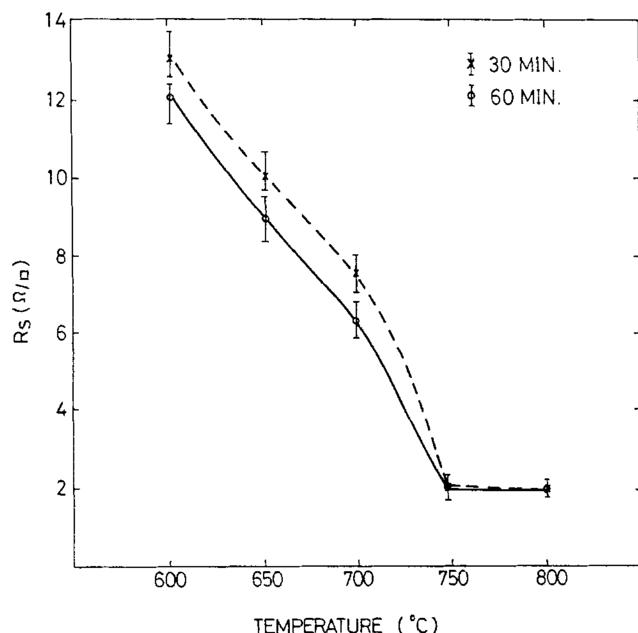


Fig. 2. Measured sheet resistance of the silicided n^+ polysilicon as a function of temperature in the first anneal for 30 min (dashed line) and 60 min (solid line).

For comparisons, the Mo/Ti bilayer structure (3) and the Ti monolayer structure were adopted in another group of wafers to form $TiSi_2$. They went through the same process in the same ambient. The AES was also applied to investigate the annealed samples.

To investigate the lateral growth (6) in the $TiSi_2$ formation using the trilayer structure, a group of p-type (100) wafers were oxidized to form a 100 nm SiO_2 layer. Then the wafers were patterned and etched to form long SiO_2 strip lines. To simulate the n^+ source/drain junction formation, the wafers were subjected to the $POCl_3$ diffusion to form n^+ single Si region with a resistance of 120 Ω/□. After the trilayer structure was formed, different annealing processes were applied to form $TiSi_2$ in the n^+ region. After stripping the Si layer, the Mo layer, and the unreacted Ti layer, SEM was applied to investigate the lateral formation. The resistivity of the resultant $TiSi_2$ was monitored from the accompanying samples of bare Si wafers and polysilicon/SiO_2/Si wafers.

Results and Discussion

The measured sheet resistance of the silicided n^+ polysilicon layer after the first annealing process is shown in Fig. 2 as a function of temperature. These data, which were taken from chips on different wafers and in different runs, have consistently shown that a low resistance of 2 Ω/□ can be obtained after annealing above 750°C for either 30 or 60 min in an N_2-flowing open tube. Below 750°C, the resistance is larger than 2 Ω/□ and is decreased with the increase of the annealing time.

The above resistance feature after the first anneal can be understood from the typical AES profiles of the silicided polysilicon as shown in Fig. 3 for the anneals performed at 600°, 650°, and 750°C for 30 min. More oxygen atoms and less titanium atoms are found in the samples annealed at a lower temperature. This means more oxide components and less $TiSi_2$ components in the polysilicon. The resultant resistivity, of course, is higher. Note that the oxygen atoms which react more easily with the samples annealed at a temperature lower than 750°C, are from contaminations both during the evaporation process and after the first anneal, but not during the first annealing process, as will be verified later.

After the second anneal at 800°C for 30 min in an N_2-flowing open tube, those samples annealed above 750°C in the first anneal show a negligible change of sheet resistance and still keep the metallic shining on the surface of the silicided n^+ polysilicon. However, the samples annealed below 750°C in the first anneal show a significant increase in resistance value even up to infinity. The surface becomes blue and no metallic shining can be observed.

Based upon the explanation of the resistance feature after the first anneal, the above results can be explained as follows. If the first annealing temperature is below 750°C, some silicide compounds besides $TiSi_2$ are formed. As compared to $TiSi_2$, these compounds may react more easily with the residual oxygen in the second annealing N_2 ambient to form SiO_2 and titanium oxides. These oxide components significantly increase the sheet resistance of the silicided polysilicon. On the other hand, if the first annealing temperature is raised above 750°C,

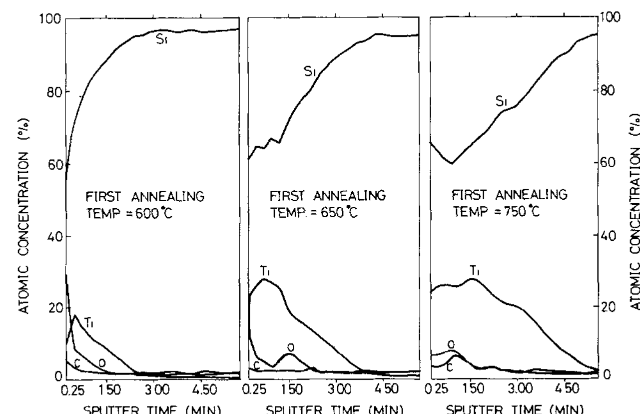
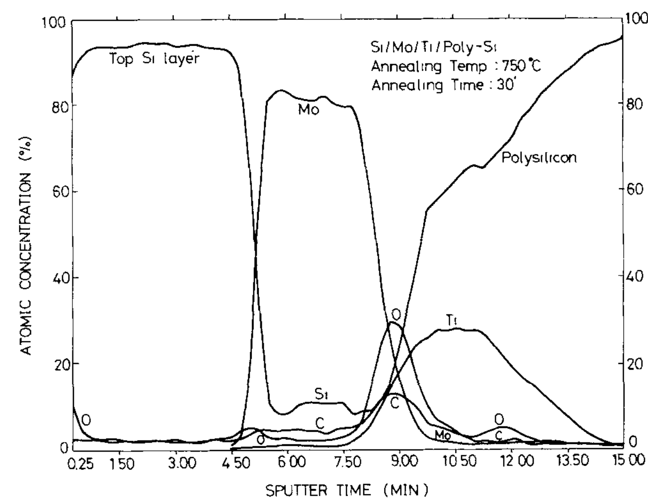


Fig. 3. AES depth profiles of the silicided n^+ polysilicon annealed for 30 min at (a) 600°C; (b) 650°C; (c) 750°C.



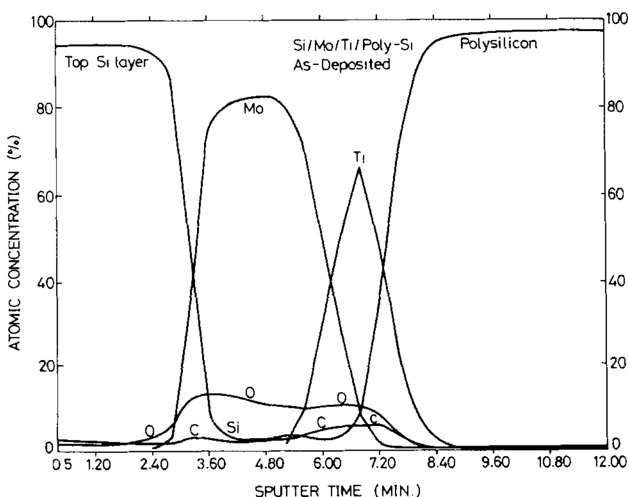


Fig. 4. AES depth profiles of the Si/Mo/Ti/poly-Si structure (a) annealed at 750°C for 30 min; (b) as-deposited.

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stable $TiSi_2$ is formed, and the resistance is lowered to 2 Ω/□. In this case, the second anneal in an N_2 ambient has a negligible effect on the silicided polysilicon. Therefore, using the proposed Si/Mo/Ti trilayer, the second anneal is not necessary, if the first annealing temperature is above 750°C.

According to our observations, the top 100 nm Si layer is very effective in preventing residual oxidants and impure gases in an N_2 ambient from reaching the bottom Ti layer. Since nitrogen and oxygen still can react with the evaporated Si layer at temperatures below 800°C, a thin nitride or oxide layer may be formed on the surface of the Si layer at the beginning of the first anneal. With the aid of this nitride or oxide layer, only a very limited amount of residual oxidants and impure gases may enter the Si layer, which then are trapped within the Si layer by reacting to the Si atoms. Thus, residual oxidants and impure gases in the first annealing N_2 ambient can hardly reach the Ti layer.

The effectiveness of the top Si layer in blocking residual oxidants and impure gases can be realized by comparing the AES profile of the annealed trilayer structure in Fig. 4a to that of the as-deposited film in Fig. 4b. It is seen that the interior of the top Si layer remains unchanged after annealing, being free from any external impure elements. Note that the oxygen atoms at the Mo/$TiSi_2$ interface, as seen in Fig. 4a, are due to contamination from the Mo or Ti target, and the evaporator chamber during the evaporation process, because they are also detected in the as-deposited Mo and Ti films, as seen from Fig. 4b. Some carbon atoms are also found in the as-deposited Mo and Ti films. However, the carbon contamination source has not yet been identified.

Because of the insulating effect of the top Si layer, a stable $TiSi_2$ silicide with a low resistance of 2 Ω/□ can be formed at an annealing temperature above 750°C in an N_2 open tube instead of a stringently controlled Ar or H_2 ambient. Furthermore, the $TiSi_2$ silicide formed in a conventional N_2-flowing open tube is highly environmentally insensitive. This insensivity leads to good uniformity obtained among different wafers and different runs in our experiments.

Without the top Si layer, the Mo/Ti bilayer structure was subjected to the same annealing process in the same N_2 ambient. The resultant resistivity of the silicided n^+ polysilicon is significantly increased even up to infinity. Evidently, the residual oxidants in an N_2 ambient may easily penetrate the Mo layer and react with the bottom Ti layer to form the titanium oxides. The AES profile of the Mo/Ti/poly-Si structure annealed at 750°C for 30 min in an N_2 ambient is shown in Fig. 5a. It is seen that the residual oxygen has oxidized both Mo and Ti films and $TiSi_2$ cannot be well-formed. The oxidized Mo layer is not seen in this profile, because it was quickly etched out

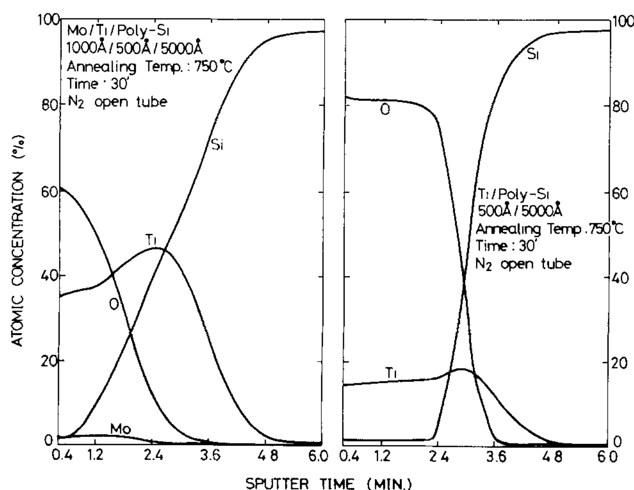

Fig. 5. AES depth profiles of (a) the Mo/Ti/poly-Si structure; (b) the Ti/poly-Si structure, both subjected to the same annealing process in an N_2-flowing open tube.

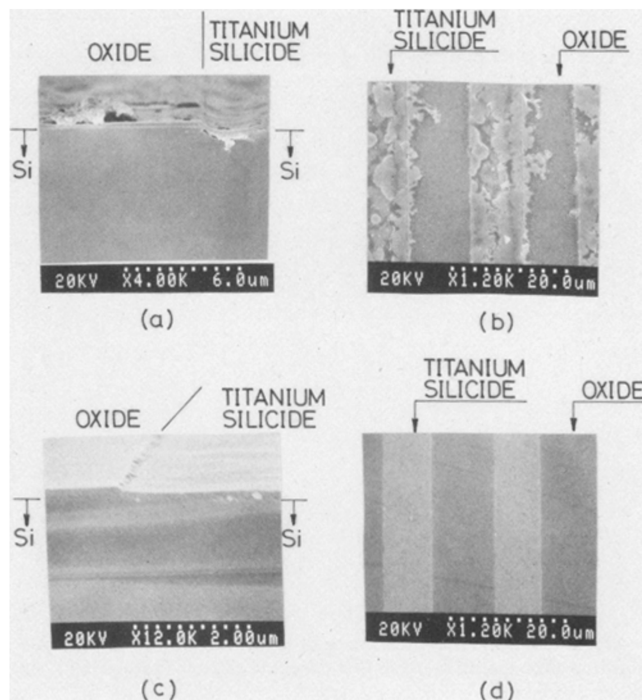

Fig. 6a. SEM cross-sectional view; b. SEM top view of the silicided single silicon subjected to 750°C 30-min annealing; c. SEM cross-sectional view; d. SEM top view of the silicided single silicon subjected to 750°C 15-min annealing.

during the preetching cycle. The depth profile of Ti/poly-Si structure subjected to the same annealing process is also shown in Fig. 5b. It can be seen that the Ti film has been more severely oxidized, and good quality $TiSi_2$ cannot be formed.

It is found that the middle 100 nm Mo layer in the trilayer structure is efficient in isolating the top Si layer from the Ti layer, because the Mo-Si reaction is not significant below 800°C, as may be seen from the depth profile in Fig. 4a. Therefore, the reaction between Si layer and Ti layer, which may interfere with the silicidation in polysilicon, can be avoided.

In this study, the ambient temperature of 750°C for stable $TiSi_2$ formation is higher by 50°C than that reported (1). This temperature increase may be attributed to the decrease of the diffusion coefficient of Si in the Ti film, which may be caused by the Mo atoms in the evaporated Ti film. Due to the substrate heating during the evaporation process, Mo atoms are very likely to enter the Ti film as may be seen from the profile in Fig. 4b. The carbon contamination in the Ti film may also lead to the decrease of the diffusion coefficient. More work will be done to find out the actual mechanism of this temperature increase.

The group of wafers used to monitor the interaction between Ti and SiO_2 were investigated after etching away the Si and Mo layer and the unreacted Ti layer. No metallic luster or any other physical changes on the oxide surface were observed, even in those samples with the first annealing temperature as high as 800°C. The index of refraction measured by an ellipsometer was 1.45, the same as that before silicidation. However, without the top Si layer, all samples with the Mo/Ti bilayer structure were found to have a metallic luster on the oxide surface after the first anneal in an N_2 ambient. Although the actual structure and the formation mechanism of the metallic luster have not yet been clear, we believe that the top Si layer is capable of preventing the generation of the metallic luster.

The SiO_2 thickness loss after the first anneal is listed in Table I for annealing temperatures from 600° to 800°C in 50° increments. As compared to the data provided by Ting *et al.* (4), the SiO_2 thickness loss is less than one-half of the loss in the $TiSi_2$ formation with a monolayer struc-

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Table I. Oxide thickness loss after the first anneal at various temperatures in an N_2 ambient

Annealing temperature	Time (min)	Loss of oxide thickness (nm)
600 °C	30	4.9 ~ 8.0
	60	7.6 ~ 9.1
650 °C	30	7.2 ~ 10.2
	60	12.1 ~ 14.5
700 °C	30	17.4 ~ 22.6
	60	17.3 ~ 25.3
750 °C	30	20.5 ~ 24.3
	60	22.4 ~ 25.9
800 °C	30	27.0 ~ 29.5
	60	28.2 ~ 30.5

Table II. The measured resistance of the silicided silicon from three different anneals employed to study the lateral growth

Annealing condition	Sheet resistivity (Ω/□)	
	N^+ poly-Si	N^+ single Si
750 °C, 30min.	2.2	1.8
750 °C, 15min.	2.4	1.8
750 °C, 15min. + 600 °C, 4hr.	2.0	1.8

ture in an Ar ambient at the same ambient temperature. From the above results, it can be realized that the reaction between Ti and SiO_2 in the trilayer structure is weakened. This is possibly due to the Mo atoms and the carbon atoms in the Ti film, as mentioned before. The other possible reason for smaller oxide loss is the small thickness of the Ti film in the trilayer structure.

Three different annealing processes were performed to investigate the lateral formation of $TiSi_2$ in the trilayer structure. It is shown that the annealing at 750°C for 30 min leads to a severe lateral growth as may be seen from the SEM cross-sectional view in Fig. 6a and the top view in Fig. 6b. Reducing the annealing time to 15 min can drastically reduce the lateral formation as may be seen from the SEM photographs in Fig. 6c and d. If an extra annealing at 600°C for 4h is performed, the resistance in the silicided n^+ polysilicon can be reduced from 2.4 to 2.0 Ω/□, as listed in Table II, without affecting the lateral formation. The real cause for the reduced lateral growth in a short-time 750°C anneal has not been definitely identified yet. But we believe that it is the same cause as that which explains the higher silicidation temperature.

Conclusions

Because the top 100 nm Si layer is highly efficient in preventing residual oxidants and impure gases from reaching the bottom Ti layer, and, because the middle 100 nm Mo layer is effective in eliminating the undesired reaction between Si layer and Ti layer, the proposed Si/Mo/Ti trilayer structure has been shown to be able to thermally form high quality $TiSi_2$ silicide on n^+ polysilicon in the first anneal above 750°C in a conventional N_2-flowing open tube. No stringently controlled H_2 or Ar ambient is required. The resultant silicided n^+ polysilicon layer has shown a low sheet resistance of 2 Ω/□, as well as high environmental insensitivity and good reproducibility. These features lead to low process cost, high yield, and easy process control.

We have also found that the interactions between Ti and SiO_2 are weakened so that the SiO_2 thickness loss is reduced. Moreover, no significant lateral growth was found in samples annealed at 750°C for 15 min. From these initial observations, we believe that an optimal process can be found to obtain acceptably small oxide loss and lateral growth.

Based upon the results of this study, it is felt that the same or similar trilayer structures can also be applied to other thermally formed silicides to reduce their environmental sensitivity and to decrease their process cost.

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