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New platinum silicide formation method using reaction between platinum and silane

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The new Pt silicide formation method using the reaction between Pt film and SiH_4 has been proposed. It has been found that Pt silicide is formed by the reaction with SiH_4 at a low temperature range of 250–400 °C. Parabolic relationships of silicide growth using the reaction with SiH_4 as well as the growth using the reaction between Pt and substrate Si are confirmed. Pt silicide formation with SiH_4 is less influenced by oxygen contamination than the formation by the reaction between Pt and substrate Si.

I. INTRODUCTION

Pt (platinum) films are suitable for use as ohmic or Schottky barrier contact electrode in Si integrated circuits.[1–4] The kinetics of the reaction between Pt and Si have been investigated by many workers[5–10] to obtain stable contact. It is well known that Pt films react with Si over a wide temperature range. This reaction is a drawback in the fabrication of fine-pattern Si devices, since it erodes the Si layer and degrades the shallow junction. To prevent Si layer erosion, Pt silicide film formation methods,[11] such as coevaporation of Pt and Si, have been suggested. However, the coevaporation method is unsuited for control of the stoichiometry of Pt and Si.

The purpose of the present work is to propose the Pt silicide formation method which supplies Si from SiH_4 to reduce the erosion of Si. First, it is described that Pt reacts with SiH_4 and that Pt silicides are formed at low temperature of 250–400 °C. Second, the silicide formation rate with SiH_4 is discussed, compared with the silicide formation rate by the reaction between Pt film and substrate Si (solid-solid reaction). Third, the effects of oxygen contamination on the silicide formation rates are discussed.

II. EXPERIMENT

A 200-nm-thick Pt film was deposited by electron beam evaporation under a pressure of about 3×10^{-7} Torr, except for experiments in oxygen doping into Pt films. The substrate was heated by a lamp heater over a temperature range of 25–400 °C. For the experiment in reaction with SiH_4, the substrates used were thermally oxidized Si wafers. To obtain strong adhesion between Pt and SiO_2, a 5-nm-thick Si layer was deposited by electron beam evaporation before Pt deposition. For the experiment in solid-solid reaction, the substrates used were (100) Si wafers chemically cleaned with a dilute HF solution.

SiH_4 treatment of Pt films was carried out in a low-pressure lamp-heated horizontal CVD reactor with the SiH_4-He gas system. The total gas pressure was 3.3 Torr. In order to compare the silicide formation rate using SiH_4 with that of solid-solid reaction, the experiment in reaction between Pt and substrate Si was carried out under the same He pressure of 3.3 Torr in the same reactor. Pressure was measured with an MKS Baratron pressure gauge. The surface temperature was measured with an optical pyrometer, corrected for emissivity of Pt, and the accuracy of the reaction temperature was controlled within ± 2 °C.

The compositional depth profile of silicidized film was measured by Auger electron spectroscopy (AES), and phase identification of Pt_2Si and PtSi was performed by x-ray diffraction and reflection electron diffraction methods. Small quantities of interfacial oxygen and Pt in the deposited Si were analyzed by secondary ion mass spectroscopy (SIMS, Cameca IMS-3F) using a Cs^+ ion beam.

III. RESULTS AND DISCUSSION

A. Platinum silicides formation with silane treatment

Figure 1 shows a typical x-ray diffraction spectra of the samples treated with SiH_4 at 325 °C, where the partial pressure of SiH_4, P_{SiH_4}, was 0.48 Torr. Diffraction peaks of Pt_2Si are found for a 1-min SiH_4 treatment. For a 20-min SiH_4 treatment, diffraction peaks of PtSi are found together with those of Pt_2Si; no diffraction peak of Pt is detected. Figure 2 shows AES profiles of the samples shown in Fig. 1. For a 1-min SiH_4 treatment, a Pt_2Si layer is formed at the surface side of the Pt film. For a 20-min SiH_4 treatment, a Pt_2Si layer formation proceeds, then a PtSi layer is formed from the surface side of the Pt_2Si layer.

From these results, it is evident that Pt silicides are formed by the reaction between Pt film and SiH_4 at the lower temperature than 400 °C. Here, it has been confirmed that very little SiH_4 is decomposed on the SiO_2 or Si surface at this temperature (325 °C). Since it is well known that Pt acts as a catalyst for the dehydrogenation of hydrides,[12,13] it is expected that SiH_4 will decompose to Si at the surface of Pt silicides. In order to estimate the decomposition rate of SiH_4 on a Pt layer, the deposition rate of Si on a PtSi layer was tested at 510 °C, and was compared with the rate on SiO_2 layer. Here, at this deposition temperature (510 °C), the deposition rate of Si on the SiO_2 layer was almost the same as that on the Si layer. Figure 3 shows the SiH_4 treatment time dependencies of thickness of Si deposited on a PtSi layer and on a SiO_2 layer at 510 °C in SiH_4 partial pressure of 0.48 Torr. Here, prior to Si deposition on a PtSi layer, the PtSi was formed on a Si substrate by the solid-solid reaction at

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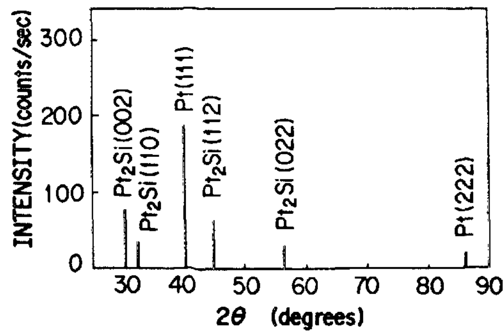


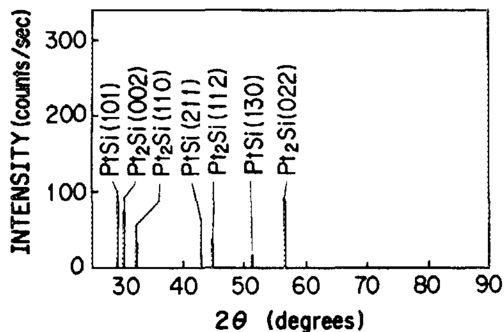
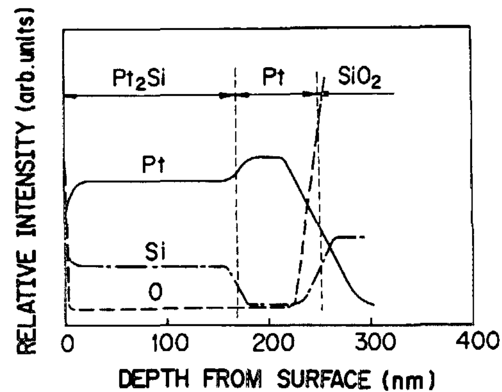


FIG. 1. X-ray diffraction pattern (Cu kα radiation) of Pt films treated with SiH_4 ambient of P_{SiH_4} of 0.48 Torr at 325 °C for (a) 1 min and (b) 20 min.



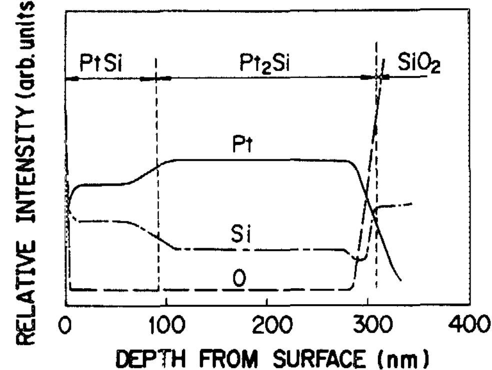


FIG. 2. AES depth profiles of the samples of Figs. 1(a) and 1(b).

600 °C and the entire Pt layer was consumed in the PtSi formation. From Fig. 3, it is found that the initial deposition rate of Si on a PtSi layer is estimated to be ten or more times larger than that on a SiO_2 layer, although the difference of the deposition rate between on PtSi and on SiO_2 decreases with increasing treatment time. This result suggests that the larger deposition rate of Si on PtSi layer is caused by the catalytic effects of Pt and the time dependency of the deposition rate is due to the diffusion of Pt into Si deposition layer from PtSi. From the SIMS measurement of the Si deposited film on the PtSi layer, Pt concentration in the Si deposited film near the PtSi layer was found to be about 10^{19} cm^{-3}. If the decomposition rate of SiH_4 is assumed to be proportional to Pt concentration, the decomposition rate on Pt or Pt silicides layer can be estimated to be 10^4 times or more times larger than that on a Si or a SiO_2 layer. This result suggests that the decomposition of SiH_4 is strongly promoted by the catalytic effects of Pt.

Figure 4 shows the partial pressure of SiH_4, P_{SiH_4} dependence of platinum silicides thickness. Here, SiH_4 treatment time and temperature were fixed to typical conditions of 5 min at 275 °C for Pt_2Si and of 6 min at 350 °C for PtSi, respectively. Under present conditions, Pt_2Si and PtSi thicknesses are independent of P_{SiH_4}, as shown in Fig. 4. This means that the limiting process of Pt silicide formation using SiH_4 is not surface adsorption of SiH_4 but the reaction between Pt and Si. Considering the results shown in Figs. 3 and 4, a monolayer, or very thin layers, of Si is expected to be deposited on the surface of Pt or Pt silicides layer, although the presence of Si layer on Pt or Pt silicides has not be clarified by AES measurements as shown in Fig. 2. Furthermore, it was confirmed that Pt silicide thickness does not change even when the sample is heat treated for 30 min at 400 °C in N_2 after treatment with SiH_4, which also strongly supports the model that the thickness of Si formed on Pt or Pt silicides layer is very thin.

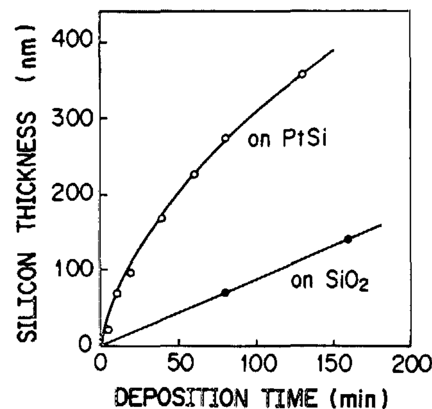


FIG. 3. Time t dependence of deposited Si thickness x at temperature of 510 °C in P_{SiH_4} of 0.48 Torr.

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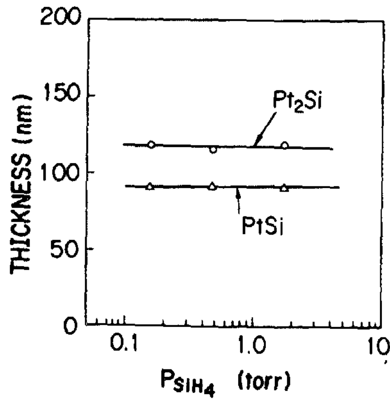
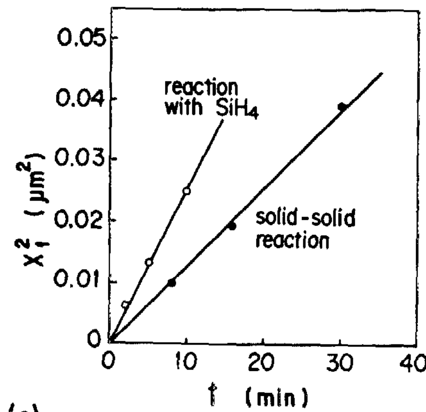


FIG. 4. P_{SiH_4} dependence of Pt silicide thickness formed with SiH_4. Pt_2Si and PtSi are formed with treatment for 5 min at 275 °C and for 6 min at 350 °C, respectively. Here, Pt was deposited at room temperature (25 °C).

From these results, it is suggested that the Pt silicide is formed with SiH_4 treatment through the following processes: (i) very thin layer of Si is formed on Pt or Pt silicide layer with decomposition of SiH_4 promoted by the catalytic effects of Pt. (ii) Pt silicide is formed by the reaction between the surface Si and the Pt. (iii) This reaction proceeds until all Pt is consumed to form the final phase of PtSi.



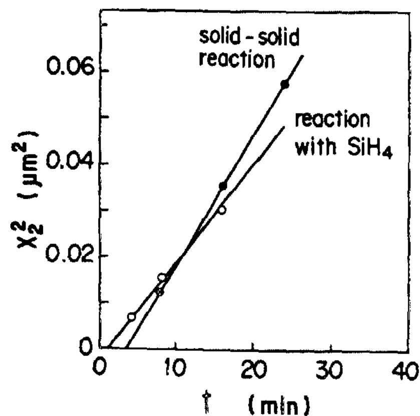


FIG. 5. The relationship between the square of Pt silicides thickness and treatment time t at the typical treatment temperature. (a) Pt_2Si thickness x_1 in the sample treated at 275 °C, and (b) PtSi thickness x_2 in the sample treated at 350 °C. Here, Pt was deposited at room temperature (25 °C). P_{SiH_4} was 0.48 Torr for the reaction with SiH_4.

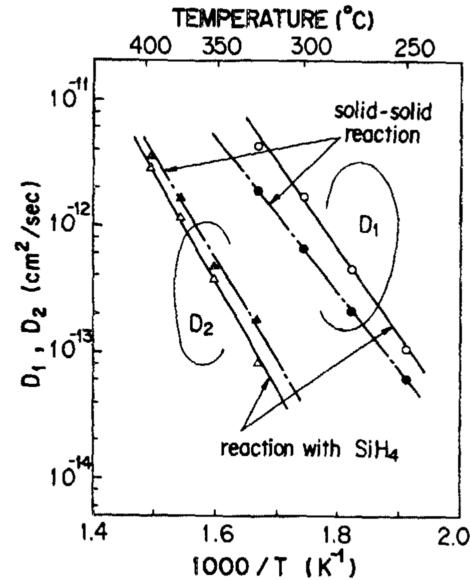


FIG. 6. Temperature dependence of diffusivities for silicide formation. D_1 and D_2 are the diffusivities for Pt_2Si formation and PtSi formation, respectively. Here, Pt was deposited at room temperature (25 °C). P_{SiH_4} was 0.48 Torr for the reaction with SiH_4.

B. Reaction rate of platinum silicide formation with silane

Figures 5(a) and 5(b) show SiH_4 treatment time dependence of Pt_2Si thickness and PtSi thickness, respectively, together with data obtained from the solid–solid reaction. Pt_2Si thickness, x_1 follows the equation $x_1^2 = D_1 t$ for the reaction with SiH_4 as well as the solid-solid reaction, where D_1 is the diffusivity of diffusion species (Pt) in Pt_2Si formation[14] and t is the SiH_4 treatment time. The D_1 is much larger for the reaction with SiH_4 than for the solid-solid reaction. PtSi thickness, x_2 is approximated by $x_2^2 = D_2(t - t_0)$, where D_2 is the diffusivity of diffusion species (Pt and/or Si) in PtSi formation and t_0 is the time required for the formation of Pt_2Si.[9] The slope of the linear relation for PtSi formation is almost the same for the reaction with SiH_4 and the solid-solid reaction as shown in Fig. 5(b), although t_0 of the solid-solid reaction is about three times larger than that of the reaction with SiH_4 according to the difference of D_1.

Temperature dependencies of diffusivities D_1 and D_2 are shown in Fig. 6. Activation energies of D_1 and D_2 are found to be 1.3 ± 0.2 and 1.5 ± 0.2 eV, respectively, while the values are almost the same for the reaction with the SiH_4 and the solid-solid reaction. These activation energies are in agreement with those reported by many investigators[6,8,9] for solid-solid reaction. Therefore, the basic mechanism of silicides formation using SiH_4 is considered to be the same as that of solid-solid reaction. Whereas the value of D_1 obtained for the reaction with SiH_4 is twice or three times larger than that of the solid-solid reaction, although both values of D_2 are very close. This behavior is discussed in the next section.

From these results, it is confirmed that Pt silicides growth using the reaction with SiH_4 obeys parabolic laws in almost the same way as solid-solid reaction does. As Si used for silicide formation is supplied from SiH_4, erosion of substrate Si can be neglected at these low temperatures.

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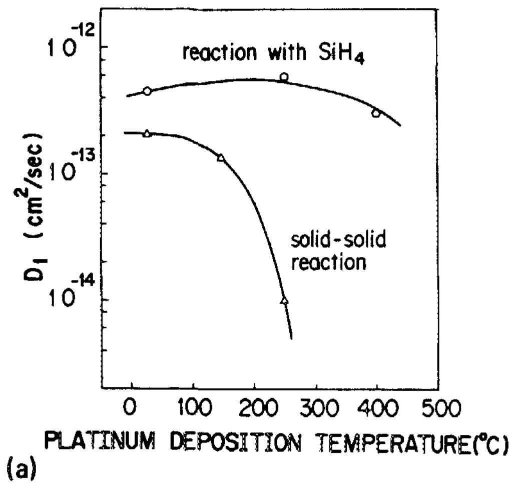


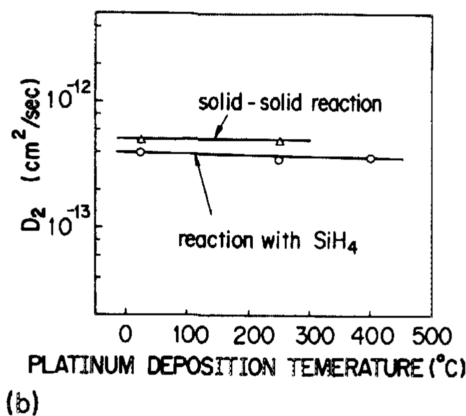
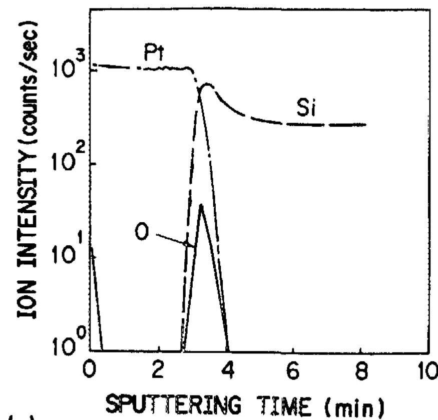


FIG. 7. Plots of diffusivity D_1 and D_2 vs substrate temperature during Pt deposition. (a) D_1 for Pt_2Si formation at 275 °C and (b) D_2 for PtSi formation at 350 °C. Here, P_{SiH_4} was 0.48 Torr for the reaction with SiH_4.

C. Effects of platinum silicide formation on oxygen contamination

Diffusivities of silicide formation are expected to depend on the Pt deposition condition. For solid-solid reaction, Crider *et al.*[9] and Nava *et al.*[10] reported that oxygen contamination in Pt film reduces the diffusivity. Diffusivity of silicide formation with SiH_4 may also be reduced by oxygen contamination. Furthermore, oxygen may be contaminated at the interface between the Si substrate and the Pt deposited layer and disturb the silicide reaction. In this section, interfacial oxygen contamination effects are clarified and the effects of oxygen in Pt are discussed compared with those of solid-solid reaction.

Dependence of diffusivities for Pt_2Si formation and PtSi formation, D_1 and D_2, on substrate temperature during Pt deposition are shown in Figs. 7(a) and 7(b). D_1 and D_2 for the reaction with SiH_4 are independent of Pt deposition temperature. On the other hand, D_1 for solid-solid reaction depends strongly on Pt deposition temperature, although D_2 is independent of it. Figures 8(a) and 8(b) show oxygen depth profiles in the samples; Pt films are deposited on the (100) Si surface at the substrate temperatures of 25 and 250 °C. It is found that the much more oxygen is involved at the interface between Pt and Si for the sample prepared at the higher Pt deposition temperature. From Figs. 7 and 8, it is assumed



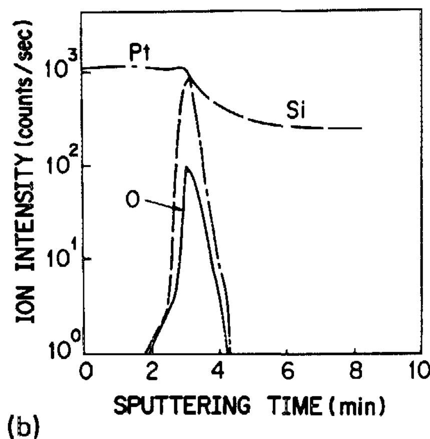


FIG. 8. Oxygen depth profiles, which are measured with SIMS, in the samples that Pt films are deposited on (100) Si at (a) 25 °C and (b) 250 °C.

that the interfacial oxidized layer suppresses solid-solid reaction to form Pt_2Si and reduces diffusivity D_1, since the Pt_2Si must be formed by the reaction through this interfacial oxidized layer. As a result, it is suggested that diffusivities for the reaction with SiH_4 are independent of the Pt deposition temperature because there is no interfacial oxidized lay-

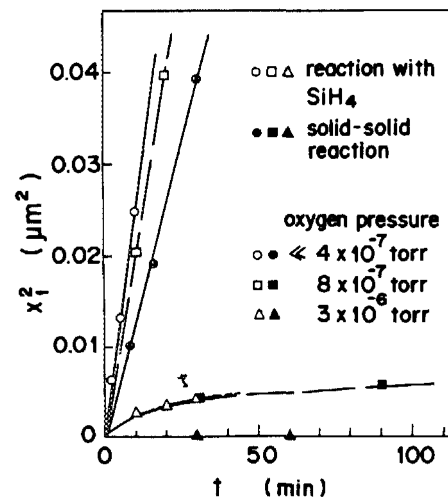


FIG. 9. The relationship between the square of Pt_2Si thickness x_1 and treatment time t for the Pt films deposited in various oxygen pressure at room temperature. Here, the samples were treated at 275 °C. For the reaction with SiH_4, P_{SiH_4} was 0.48 Torr.

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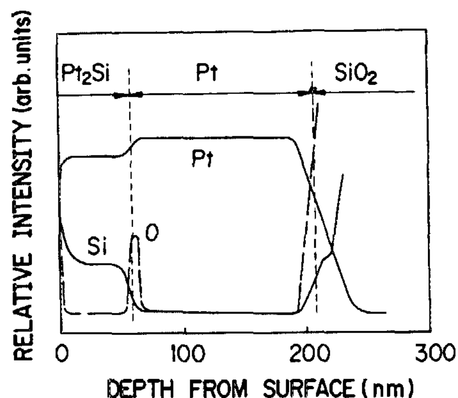

FIG. 10. An AES depth profile of the sample treated for 20 min in P_{SiH_4} of 0.48 Torr at 275 °C, where Pt was deposited in oxygen pressure of 3×10^{-6} Torr.

er at the surface of Pt. Diffusivity D_1 for Pt_2Si formation for the solid-solid reaction may become almost the same as that for the reaction with SiH_4, if there is no interfacial oxidized layer.

Next, the effects of oxygen contamination during Pt deposition on Pt silicide formation are discussed. Figure 9 shows treatment time dependencies of the square of Pt_2Si thicknesses for reaction with SiH_4 and for solid-solid reaction, respectively, where Pt was evaporated under various degrees of oxygen pressure. It is found that the Pt_2Si formation rate for solid-solid reactions is reduced by increasing oxygen pressure during Pt deposition, as reported by Crider *et al.*[9] The Pt silicide formation rate for reaction with SiH_4 is also reduced, while the influence of oxygen contamination on Pt_2Si formation rate for the reaction with SiH_4 is much less than that on solid-solid reaction. The reduction of the formation rate for the reaction with SiH_4 cannot be explained by the interfacial oxidized layer effects described above. Figure 10 shows the oxygen depth profile of a sample treated for 20 min in SiH_4 partial pressure of 0.48 Torr at 275 °C, where Pt was deposited in an oxygen pressure of 3×10^{-6} Torr. Pileup oxygen is found at the interface between Pt and Pt_2Si, while the similar phenomena have been reported by Nava *et al.*[10] for the reaction between oxygen-implanted Pt films and Si substrates. This pileup may be caused by oxygen contained in Pt film. It is considered that Pt silicide formation with SiH_4 is suppressed by the pileup of oxygen at the interface between Pt and Pt_2Si.

From these results, it is confirmed that the effects of oxygen on the Pt silicide formation with SiH_4 are much less than those of the solid-solid reaction as the former reaction is not influenced by Pt-Si interface contamination.

IV. CONCLUSION

It has been confirmed that Pt reacts with SiH_4 and forms platinum silicides at low temperature of 250–400 °C enhanced by the Pt catalytic effect. Pt silicide formation with SiH_4 follows a parabolic relationship between silicide thickness and SiH_4 treatment time. In comparison with Pt silicide formation by the solid-solid reaction, Pt silicide formation by reaction with SiH_4 has the following merits: (i) Pt silicide formation using SiH_4 is not influenced by Si-Pt interface contamination. (ii) It is less influenced by oxygen contamination during Pt deposition than in solid-solid reaction. (iii) Erosion of Si from the substrate can be reduced without limiting Pt silicide thickness since Si used for the silicide formation is supplied from SiH_4. Therefore, the platinum silicide formation with SiH_4 will be useful not only for the contact electrode on shallow diffused layer of fine pattern Si integrated circuits, but also for gate and interconnect metallization.

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