Transmission electron microscopy investigation of silicide formation on slightly oxidized silicon substrates

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The formation of PtSi and Pd₂Si on chemically cleaned and on slightly oxidized Si substrates had been investigated by TEM with cross-sectional specimens. The oxide has been found to influence the silicide-Si interface roughness, the silicide surface roughness, and the corrosion behavior of the silicide layer. The formation of PtSi is more sensitive to the presence of oxide than Pd_2Si and may even be suppressed. Remnants of the oxide are identified within the silicide using Auger sputter profiling technique. They can be interpreted as diffusing markers and provide information about the diffusing atomic species. Results of such marker experiments for formation of Pd₂Si and PtSi are discussed.

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INTRODUCTION

Silicide contacts on silicon devices are rapidly gaining importance in integrated circuit technology. A technically useful contact has to meet many requirements. Of particular importance are small and uniform penetration depth, suitable electrical properties, good adherence, and corrosion behavior and high reproducibility. Silicide layers are formed by a solid-state reaction between the Si substrate and a metal layer at elevated temperatures, so that the final silicide-Si interface is usually not identical with the original metal-Si interface. Impurities and the native oxide, which are always present on the Si surface before deposition of the metal layer, may dominate electronic and structural properties of the metal-Si interface, but need not be present in the silicide-Si interface. Consequently the properties of the silicide-Si interface are expected to be controlled mainly by the properties of the constituents of the system^{1,2} as well as by structural parameters of the interface such as steps or interfacial dislocations.³

While impurities may not directly govern the final properties of the silicide-Si interface, the formation of silicides, e.g., the reaction kinetics and structural properties of the silicide, can be significantly influenced by the presence of impurities.⁴ This is particularly well documented for platinum silicide, 5-10 where it has been shown that the presence of oxygen on the Si substrate, in the deposited Pt layer, or in the annealing atmosphere can control the reaction kinetics and the final reaction products in the Pt-Si system. Similar observations have been made for other silicide systems. So far, most attention has been focused on the effects of impurities, particularly oxygen, contained in the asdeposited metal films or in the annealing atmosphere, whereas the effects of impurities in the metal-Si interface, particularly the native SiO₂, have been investigated to a lesser extent. Native oxide has been shown to slow down or even inhibit the reaction between Pt and Si, ¹¹ or give rise to an incubation time for the reaction in the cases of the Cr-Si and Pd-Si systems.^{12,13} In this paper,

results from transmission electron microscopy (TEM) are reported for the formation of PtSi and Pd₂Si on substrate wafers covered with a native oxide layer ~1 and ~ 3-nm thick. By using cross-sectional TEM, the interface morphology can be examined in considerable detail and our results reveal significant effects depending on the amount of the oxide present. In addition, Auger spectroscopy (AES) has been used to observe directly the oxygen distribution after silicide formation. At the end, we will discuss how the position of the oxide remnant can be used as a marker to indicate the relative mass transport of metal and Si atoms during silicide formation.

EXPERIMENTAL

Four Si wafers (*n*-type, 10 Ω cm, {111} oriented) were first degreased in organic solvents and then boiled in a mixture of $NH_4OH: H_2O_2: H_2O = 1:2:7$. This procedure slightly oxidizes the Si and leaves an oxide layer roughly 3-nm thick. After rinsing with distilled water, two wafers were dipped in buffered HF to remove all oxide and immediately loaded into the evaporation unit, together with the other two wafers. Two wafers thus were only covered with the unavoidable native oxide of ~1-nm thickness and henceforth will be called clean, whereas the other two wafers were covered with a thicker (~3 nm) and probably rather non-uniform oxide and henceforth will be called oxidized. 50 nm of Pd or Pt were then evaporated with an electron-gun evaporator onto a clean and an oxidized wafer, respectively. All four wafers were then annealed at 400 °C for 1 h in a He atmosphere in order to form PtSi and Pd₂Si.

Samples from the reacted wafers were examined using TEM both in the conventional way (electron-beam perpendicular to silicide surface; flat-on sample) and in cross section (electron-beam parallel to silicide surface; edge-on sample). In the first case, the samples were chemically thinned from the back side; in the second case, the preparation procedure outlined in Refs. 14 and 15 were followed. A JEOL 200B microscope operated at 200 kV was used for the TEM investigation.

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RESULTS

Palladium silicide

Figure 1 shows a flat-on view of the silicide films formed on the clean and the oxidized substrates where Pd₂Si was obtained as deduced from the diffraction patterns. The Pd₂Si on the clean substrate grew mostly epitaxially which is commonly observed on (111) Si.¹⁶ The Pd₂Si layer appears to be rather uniform and the average size of the sub-grains is ~40 nm. The Pd₂Si on the oxidized wafer is still partially epitaxial to the substrate, but much less so than on the clean substrate. The silicide has an average grain size of ~40 nm and appears to be rather non-uniform in thickness. Its general appearance is quite similar to that of Pd₂Si formed *in situ* on a heated substrate.¹⁷

Cross-sectional TEM reveals major differences between the two cases (Fig. 2). For the clean wafer the Pd₂Si-Si interface is very smooth and well defined. The silicide surface is somewhat rough with a peak-to-peak amplitude of ~15 nm. In contrast, the Pd₂Si formed on the oxidized surface has a rather rough (amplitude ~10 nm) and often ill-defined interface and a very rough (amplitude ~ 30 nm) surface. Most striking, however, are irregularly shaped inclusions, showing bright contrast, arranged in an irregular line parallel to, and located at about 1/2-2/3 silicide thickness below the surface. The contrast of these inclusions is reminiscent of that of voids: indeed, small SiO₂ inclusions in a Pd₂Si matrix can be expected to exhibit a contrast similar to that of voids. However, it will be shown later when we describe the AES result that they are related to the oxide layer originally present on this wafer.

Following this observation, one would expect to find similar features, albeit smaller, in the Pd₂Si



FIG.2. (a) Cross-sectional view of Pd_2Si on the clean substrate. (b) Cross-sectional view of Pd_2Si on the oxidized substrate.

formed on clean wafers, because in this case also a thin oxide layer was present. A systematic search for these inclusions among old and recent micrographs indeed showed the presence of very small inclusions at approximately the same position as in the oxidized wafer. These inclusions were not only found in the clean samples discussed in this paper but also in Pd_2Si formed on chemically cleaned {100} Si; Fig. 3 gives an example. The inclusions are not easy to see because their size is





FIG.1. (a) Pd₂Si film on the clean substrate. (b) Pd₂Si film on the oxidized substrate.

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FIG. 3. Band of oxide remnants (between arrows at about 1/4-1/3 from the silicide-Si interface) in Pd₂Si on a {100} oriented clean substrate.

comparable to the resolution limit of the microscope. Consequently, they are only visible under favorable imaging conditions and probably have been overlooked so far.

The presence of oxide in the Pd₂Si layer was checked by measuring the in-depth composition distribution using Auger sputter profiling technique. This was carried out in a scanning Auger microprobe (PHI Model 590). The primary electron beam was operated at 8 keV with a diameter of 5 µm, so that the signal was obtained by averaging over an area comparable to TEM. The Ar ion energy used was 2 keV with a beam intensity chosen to yield a sputtering rate of about 1 Å/s, these conditions were used to minimize the sputtering artifacts¹⁸ while maintaining a reasonable sputter rate. The composition distribution was obtained by monitoring sequentially the Pd MVV, Si KLL, and O KLL Auger signals during sputtering. The peak-to-peak height ratio of the Pd and Si spectra was converted to the atomic percentage using a previous calibration for the Pd-Si system.¹⁹ Since a similar calibration was not available for oxygen, its concentration was calculated using the elemental sensitivity factors. Thus the absolute concentration of oxygen given here is only semi-quantitative, although the relative levels of oxygen in different samples are more accurate.

The composition profiles observed in the clean and oxidized samples are shown in Fig. 4. The presence of oxygen in both samples is clearly observed since the oxygen level is several times higher than the detection limit of about 0.2 at. %. Compared with the clean wafer, the oxidized wafer contains about twice the amount of oxygen and the distribution is less uniform. Integrating the oxygen distribution yields an amount equivalent to about 20 Å of SiO₂ in the oxidized sample and about 10 Å in the clean sample. These results indicate that the oxygen observed in the silicide layer is related to the oxide remnants. To find the actual location of the oxide, one has to consider the effect of surface roughness on the in-depth profile. The extent of this effect can be seen from the broadening of the Pd₂Si-Si interface in these two samples. Defining the interface width as that between the 85% to 15% of Pd composition, the oxidized sample has a width of 35 vs 20 nm for the clean sample. These values agree with the total roughness of the silicide layers observed by TEM, reflecting the broadening of the observed profiles by morphological roughness. The oxygen profile of the oxidized sample is broader than its Pd_2Si -Si interface indicating a non-uniform distribution of the oxide remnants. The observed oxygen profile can be interpreted as an overall non-uniform oxide dispersing within about 1/3-2/3 of the silicide layer.

Pd₂Si contacts have been found to degrade with time as a result of corrosion induced bubbling or peeling of the Pd₂Si layer.^{20,21} Since the corrosive reaction is induced by traces of HF in the environment, an accelerated test for corrosion resistance can be carried out



FIG. 4. Composition distributions obtained by the Auger sputter profiling technique for the oxidized and clean samples.

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FIG. 5. (a) Bubbling of Pd₂Si on the clean substrate after 3 h. (b) Bubbling and peeling of Pd₂Si on the clean substrate after 24 h. (c) Bubbling and peeling of Pd₂Si on the oxidized substrate after 0, 5 h.

simply by immersing a specimen into diluted HF. To check the effect of morphological roughness on corrosion resistance, the two Pd_2Si layers were subject to this test. Figure 5 shows that the corrosion behavior of Pd_2Si formed on a clean and an oxidized substrate is very different. Whereas the Pd_2Si formed with the clean substrate shows first signs of bubbling after ~3 h in 1% HF, the Pd_2Si formed with the oxidized substrate peeled off almost completely after only 30 min.

Platinum silicide

The differences between the clean and the oxidized substrate are even more striking than in the Pd case. Figure 6 shows a flat-on view of the layers formed. A rather uniform layer of PtSi is observed on the clean substrate with a partially epitaxial relationship to the Si matrix^{10,15} and an average grain size of ~100 nm. On the oxidized substrate the reaction is incomplete and patches of unreacted Pt are present, with irregularly shaped lumps of PtSi in between. The cross-sectional micrographs in Fig. 7 give a clear impression of these structures. On the clean wafer the PtSi-Si interface is rather rough (amplitude ~25 nm), but the silicide surface is very smooth, in accordance with earlier results.¹⁵ On the oxidized wafer, areas of unreacted Pt and lumps of PtSi are visible. Most of the PtSi lies on the Si side of what would have been the original Si-Pt interface (the position of which is given by the area ratio of the silicide and the unreacted Pt). Between the unreacted Pt and the Si occasionally a thin (~3 nm) bright band can be seen which may be identified to be the oxide layer.

Auger sputter profiling technique has been used to measure composition distribution in PtSi layers formed on Si substrates with 10-20-Å oxide²³ (but not on samples used for TEM observations in this paper). In most of the samples, the presence of oxygen was clearly ob-



FIG. 6. (a) PtSi on the clean substrate. (b) Unreacted Pt and PtSi on the oxidized substrate.

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FIG. 7. (a) Cross-sectional view of PtSi on the clean substrate. (b) Cross-sectional view of the unreacted Pt and PtSi on the oxidized substrate. (c) Enlarged view of Fig. 7(b); note the bright band between the unreacted Pt and the Si substrate.

served with its distribution concentrated at or near the surface of the PtSi layers. Analysis of the oxygen profile similar to that used for Pd₂Si shows that the oxygen is related to the oxide remnants.

As in the case of Pd₂Si one expects to see traces of the native oxide also in PtSi which was formed on a clean wafer. Unfortunately, several attempts to find the oxide layer failed, mainly because it was not yet possible to obtain cross-sectional specimens thin enough to allow an unambiguous identification of the small oxide particles. However, for reasons outlined in the discussion, the oxide layer in this case can be expected to be located close to the silicide surface which would make a detection very difficult. A better opportunity for finding the oxide layer is provided by forming PtSi using Pt and Si coevaporation on a Si substrate. In this case only a small part of the Pt will react with the substrate²⁴ and the oxide layer will be on top of that part of the PtSi which formed by reaction with the Si substrate, i.e., at a position about equal to the original wafer surface. In cross-sectional specimens prepared from PtSi formed by coevaporating Pt87Si33 or Pt55Si45, a row of small bright dots ~2 nm in size was indeed found (see Fig. 8) at a position close to the original wafer surface (which is known from the calculated penetration depth for a given composition). In accord with the general ideas put forward in this paper, these inclusions are interpreted as oxide remnants originating from the native oxide on the Si substrate.

Attempts to detect these SiO_2 inclusions in flat-on specimens have not been successful. Even if most of the PtSi on top of the inclusions is removed by ion-milling, the inclusions are not clearly visible and would be very difficult to be detected under normal circumstances.

DISCUSSION

The experiments reported here give not only insight into the effect of the native oxide on the interface morphology but serve also as marker experiments, 1 from which one can extract information about the ratio of the two diffusion fluxes during silicide formation. To illustrate the marker experiment, consider the case with only metal diffusing, then all silicide will be formed below the native oxide layer, and the oxide will be found on top of the silicide. On the other hand, if only Si were to diffuse, the oxide layer would be found at the Sisilicide interface. More generally, if both species diffuse, the oxide layer will be somewhere between the extreme positions, provided that the silicide-forming reaction takes place at the two interfaces only. Oxide particles therefore act as straightforward markers (provided that the interface drag¹ can be neglected). In comparison, knowledge of the original surface position can only provide information on the volume change during



FIG. 8. PtSi formed by co-evaporation of $\mathrm{Pt}_{67}\mathrm{Si}_{33}$ on a clean substrate.

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silicide formation but not the relative mass transport since if there is a volume change, the silicide surface will be different from the original Si surface by an amount directly given by the volume change. Oxide particles, however, can only be used in cases where the metal does not react with the oxide or diffuse through the oxide; in addition, their presence may induce changes in the reaction mechanism. Therefore it would be desirable to monitor both oxide position and original surface position at the same time, a task which can be accomplished using cross-sectional TEM in conjunction with Auger sputter profiling on specially prepared specimens. Supplementary information may be obtained by performing parallel experiments with silicon deposited on the metal substrates.

The present experiments have not been conducted as a marker experiment in the above sense, i.e., no special care has been taken to optimize the oxide surface or protect parts of the surface. Still, the position of the oxide particles in the Pd₂Si, both for clean and oxidized wafers, indicates that Pd and Si are both diffusing during Pd₂Si formation. This is in agreement with the results of other marker experiments, 25,26 where it has been found that both species are diffusing in Pd. which is in contrast to Pt or Ni, where the metal is the main diffusing species. In an earlier work using Rutherford backscattering to study Pt silicide formation, ²⁷ Pt was concluded being the primary diffusion species based on the explanation that the initial formation of PtSi at the Si-Pt₂Si interface is due to Si diffusing through PtSi to interact with Pt2Si. No marker was used to check the conclusion. In the Pt case the results of our experiments are less clear-cut. However, taking our results that formation of PtSi occurs mainly below the original Si surface and oxide remnants locate close to the silicide surface, it is reasonable to conclude that Pt is the main diffusing species, at least for the formation of Pt₂Si which precedes PtSi formation. It appears that the relative mass transports of metal and Si atoms during formation of PtSi and Pd2Si are different, an observation which so far has not been properly explained.

The effect of a thin oxide layer on PtSi or Pd2Si formation is quite different. The formation of Pd₂Si is less influenced by surface oxide or contamination than that of PtSi, where the reaction may even be suppressed. This is in agreement with earlier observations where it was found that the presence of a thin oxide layer only delays, but does not significantly change, the formation of Pd₂Si, ¹² whereas it may suppress the formation of PtSi.¹⁰ As shown in this paper, the first statement is only partially true. While the Pd₂Si layer formed on the oxidized substrate does not appear to be very different from the one on the clean substrate if conventional methods such as Rutherford backscattering or even flat-on TEM are employed, the cross-sectional TEM shows significant differences. The Pd2Si formed on the oxidized specimen had a much rougher interface and surface than the silicide on the clean substrate and it contained fairly large oxide remnants. These are not just subtle differences as illustrated by the dramatically different response to a corrosion test. The similarity between the Pd,Si formed on the oxidized substrate with that formed on a heated clwan substrate (cf. Ref. 17) sug-

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gests that heating the substrate before and during the metal deposition may lead to a slight surface oxidation or contamination of the substrate which is responsible for the silicide structures observed in this case.

From the observations reported here it can be inferred that the roughness of the PtSi-Si interface found here and also reported in an earlier paper¹⁵ is directly linked to the presence of the native oxide, present on all but sputter-cleaned samples, and that PtSi formed on a truly clean substrate would most probably have a planar interface. The same is true for Pd₂Si, although the effect of the oxide on the interface roughness is less pronounced than in the PtSi case. The results reported here on the oxide effect on interface morphology point out some of the structural concern for the use of silicides as device contacts. In addition, the oxide remnants may directly degrade the electronic properties of the junction as well as to increase the electrical resistance of the contact.

CONCLUSIONS

TEM of cross-sectional samples is a powerful investigation method capable of obtaining information not easily accessible with other methods. Using this method, it was possible to show that the presence of thin oxide layers on a Si substrate significantly affects the formation of PtSi and Pd2Si. The native oxide essentially controls the roughness of the silicide-Si interface and the silicide surface, i.e., the uniformity of the silicide layers, the corrosion behavior of the silicides, and it may also influence the electronic properties of a silicide contact. The oxide can be incorporated into the silicide and thus may serve as marker for indicating the relative mass transport of metal and Si atoms during silicide formation. It was found that in the Pd case both the Pd and Si diffuse, whereas Pt is the main diffusing species in the Pt case. The observations open the possibility of using the native oxide, or small oxide islands produced for that purpose, as markers in future experiments.

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