Formation of Palladium Silicide on Heavily Doped Si(001) Substrates Using Ti Intermediate Layer

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The formation of palladium silicide on Pd/Ti/Si systems with and without heavy B-doping has been investigated. For comparison, Pd$_2$Si was also formed on Pd/Si systems. The agglomeration of Pd$_2$Si could be retarded in Pd/Ti/Si systems with and without B-doping after annealing at 600°C. The existence of the Ti layer could improve the thermal stability of Pd$_2$Si. In addition, epitaxial or highly oriented Pd$_2$Si formed in Pd/Ti/Si systems. The two orientation relationships of Pd$_2$Si layers were identified to be Pd$_2$Si[110] $\parallel$ Si[110] and Pd$_2$Si[110] $\parallel$ Si[001], and Pd$_2$Si[001] $\parallel$ Si[110] and Pd$_2$Si[001] $\parallel$ Si[001]. The formation of strained epitaxial Pd$_2$Si layers was found in Pd/Ti/Si systems. The improvement in the thermal stability of Pd$_2$Si and the formation of epitaxial or highly oriented Pd$_2$Si in Pd/Ti/Si systems were observed with and without B-doping.

1. Introduction

Metal silicides have been fascinating materials owing to their technological application as ohmic contacts, metal gates, Schottky contacts, and interconnects. Palladium (Pd) silicide is potentially attractive from the viewpoint of contact materials for shallow junctions because Pd forms a metal-rich silicide, Pd$_2$Si,$^5$ which remains stable up to 700°C after formation at a low temperature, and the consumption of Si for Pd$_2$Si formation is smaller than those of NiSi, Ni$_3$Si$_2$, CoSi$_2$, and TiSi$_2$. In addition, Pd$_2$Si has a low Schottky barrier height for a p-type contact (0.3 eV).$^5$ However, the agglomeration of Pd$_2$Si has been a serious problem that results in the degradation of metal contact (source/drain) performance in metal–oxide–semiconductor field-effect transistor (MOSFET) applications. We previously reported that Pd$_2$Si agglomeration occurs at a temperature of 550°C in Pd/Si systems.$^3$

Epitaxial or highly oriented silicides on Si substrates have many advantages over polycrystalline silicides, such as a high thermal robustness, an improved Schottky barrier uniformity, a reduced junction shorting, and a suppressed dopant redistribution after the formation of contacts on shallow junctions. The epitaxial growth of metal silicides could be induced through either the implantation of an impurity into a Si substrate prior to metal deposition or using a metal intermediate layer between a metal film and a Si substrate. For example, the presence of BF$_2$, B, and F atoms was found to promote the epitaxial growth of NiSi$_2$ in Ni thin films on Si substrates at low temperatures.$^5,5$ Previously, we reported that the formation of an epitaxial NiSi$_2$ layer at low temperatures was due to a titanium intermediate layer in Ni/Ti/Si systems.$^6,7$ Most papers indicated that the Pd$_2$Si films grown on Si[111] showed a strong tendency toward an epitaxial single-crystal growth, while on other Si orientations, the azimuth orientation of Pd$_2$Si was completely random.$^8,9$ It has been reported that epitaxial Pd$_2$Si could be formed on Si(001) using a Ti intermediate layer.$^{10,11}$ However, there is no data on palladium silicide formation by using a Ti layer on heavily doped Si(001). As a thin silicide layer on a heavily doped junction is important for forming a shallow junction, it is necessary to clarify properties of Pd silicide thin layers for the contact application of Si MOSFETs. In this study, we investigated the growth and thermal stability of Pd silicide thin films on heavily B-doped Si(001) using a Ti intermediate layer.

2. Experimental Methods

The substrates used were n-type Si(001) with a resistivity of 0.1–10 Ω cm. After standard acid treatment, the wafers were dipped into a diluted HF solution and rinsed for 5 s in deionized water in order to remove the surface oxide and to obtain H-passivated surfaces.$^{12}$ Immediately, some wafers were loaded into the oxidation chamber at 1000°C for 2 h in order to obtain a SiO$_2$ thickness of 50 nm. Then, the ion implantation of B was performed using a BF$_3$ source with doses of 3 × 10$^{14}$ and 1 × 10$^{15}$ cm$^{-2}$ at an energy of 30 kV. After the ion implantation, a rapid thermal annealing (RTA) at 1100°C for 30 s was performed to realize recrystallization. Again, the wafers were chemically cleaned as mentioned above, while the other wafers were loaded into the vacuum chamber without ion implantation. A 10-nm-thick Pd layer or a 2-nm-thick Ti layer followed by a 10-nm-thick Pd layer was formed on the substrate by electron gun evaporation in an ultrahigh-vacuum chamber whose base pressure was below 1 × 10$^{-8}$ Pa. Hereafter, these samples were called Pd/Si or Pd/Ti/Si samples, respectively. The samples were successively annealed at 300°C in the same chamber for 10 min, and then, they were exposed to atmospheric conditions. Some samples were additionally annealed at temperatures ranging from 400 to 600°C for 30 s in N$_2$ ambient using an RTA system. X-ray diffraction (XRD) analysis using a Cu Kα source, cross-sectional transmission electron microscopy (XTEM), and scanning electron microscopy (SEM) were carried out to reveal the crystalline structures and morphology of the films. The sheet resistance of the films was measured by a linear four-point probe method.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) 2θ/θ spectra of Pd/Si and Pd/Ti/Si samples with and without B-doping after annealing at 300°C for 10 min and additional RTA at 600°C for 30 s. Two diffraction peaks at about 27.45° and 44.36° are identified as Pd$_2$Si 110 and PdSi 211, respectively. These peaks also appear on Pd/Ti/Si samples with
and without B-doping at 400–500 °C but not on the samples without a Ti layer (not shown). To increase the sensitivity for identifying the silicide phase and to determine whether the silicide film has a polycrystalline or highly oriented structure, the grazing-angle XRD was used. The grazing-angle XRD spectra clearly confirmed that polycrystalline Pd$_2$Si was predominantly formed in Pd/Si at 300 °C, as shown in Fig. 2. In contrast, in Pd/Ti/Si samples with and without B-doping, diffraction peaks of Pd$_2$Si are very weak after annealing at 300 °C. These results indicate the formation of epitaxial or highly oriented Pd$_2$Si in Pd/Ti/Si systems with and without B-doping at low and high doses of B atoms. It is considered that a Ti intermediate layer plays a role larger than that of a B impurity in the formation of epitaxial or highly oriented Pd$_2$Si.

The dependence of crystalline orientation on annealing temperature is shown in Fig. 3. Normalized intensity is obtained from all intensities in Fig. 1, which were normalized by the intensity of Si substrates and the powder diffraction intensity ratio of Pd$_2$Si 110 and PdSi 211 planes. The intensities of Pd$_2$Si 110 increase with annealing temperature.
temperature, while those of PdSi 211 remain almost constant. If it is considered that the intensity is directly proportional to the volume of silicide domains, the volume of Pd$_2$Si domain increases with annealing temperature, while the volume of PdSi domain remains almost constant. These results indicate that Pd$_2$Si and PdSi are formed during the first-step annealing at 300 °C and we suggest that the growth rate of Pd$_2$Si is markedly higher than that of PdSi as annealing temperature increases during the second-step RTA.

Figures 4(a)–4(c) and 4(d)–4(f) show SEM images of the Pd/Ti/Si and Pd/Si samples, respectively, with and without B-doping after annealing at 600 °C for 30 s. The agglomeration of Pd silicides (Pd$_2$Si and PdSi) and the Si exposed area corresponding to dark regions are clearly observed in the samples without a Ti intermediate layer. On the other hand, Si exposed regions hardly appear in the samples with a Ti intermediate layer.

Fig. 4. SEM images of Pd/Ti/Si samples (a) without doping and (b) with B-doping at $3 \times 10^{14}$ and (c) $1 \times 10^{15}$ cm$^{-2}$ after RTA at 600 °C for 30 s. Pd/Si samples (d) without doping and (e) with B-doping at $3 \times 10^{14}$ and (f) $1 \times 10^{15}$ cm$^{-2}$ after RTA at 600 °C for 30 s.

Here, we deduced the model of the dependence of interfacial reactions on annealing conditions. In general, Pd$_2$Si is formed by a diffusion-controlled process at temperatures ranging between 100 and 700 °C.8) In the case of annealing at a temperature of as low as 600 °C in Pd/Si systems, Pd atoms directly diffuse through Si and the Pd$_2$Si domain rapidly grows. As a result, pyramidal Pd$_2$Si domains consisting of pyramidal domains with wedge-shape facets are clearly observed in Fig. 5(a). The angle of the pyramidal domains is estimated to be about 120°, indicating that the facets are Pd$_2$Si 100 planes. On the other hand, the flatnesses of the Pd$_2$Si/Si interface are almost similar in the Pd/Ti/Si-undoped and Pd/Ti/Si-B-doped samples. Considering that the dominant diffusion species during the formation of Pd and Ti silicides are Pd and Si, respectively,13,14) it is considered that, during annealing for silicidation, Pd atoms should diffuse into the Si substrate through a Ti intermediate layer to form epitaxial Pd$_2$Si, and Si atoms should diffuse upward to form Ti silicides. Finally, it is considered that the stacked layer structure consisting of a Ti silicide surface layer and a Pd$_2$Si layer on a Si substrate is formed.

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Fig. 5. (Color online) Cross-sectional TEM images of (a) Pd/Si, (b) Pd/Ti/Si-undoped, and (c) Pd/Ti/Si-B-doped $1 \times 10^{15}$ cm$^{-2}$ samples after RTA at 600 °C for 30 s.
other hand, in the case of Pd/Ti/Si systems at a temperature of 600 °C, the diffusion of Pd atoms through a Ti intermediate layer is suppressed compared with that in the case of Pd/Si systems with and without B-doping. The nucleation of epitaxial Pd$_2$Si simultaneously and densely occurs. Consequently, the uniform growth of a Pd$_2$Si layer preferentially occurs, i.e., the area of {100} facets becomes small and a flat interface is formed.

Figure 6 shows the transmission electron diffraction (TED) pattern of the Pd/Ti/Si-undoped sample after annealing at 600 °C. The pattern is similar to that of the Pd/Ti/Si-B-doped (1 × 10^{15} cm$^{-2}$) sample (not shown). Since PdSi diffraction spots could not be observed in this image, we only consider Pd$_2$Si diffraction spots. We observed that Pd$_2$Si grains are highly oriented with respect to the Si substrate. The epitaxial Pd$_2$Si structures of the Si substrate were observed from TED patterns. The two orientation relationships of Pd$_2$Si layers were identified to be Pd$_2$Si[110] $\parallel$ Si[110] and Pd$_2$Si[110] $\parallel$ Si[001], and Pd$_2$Si[100] $\parallel$ Si[110] and Pd$_2$Si[001] $\parallel$ Si[001]. This result also agrees with the XRD 2θ/θ spectra of the Pd/Ti/Si system shown in Fig. 1, and this TED observation reveals that epitaxial Pd$_2$Si is formed with a double domain structure, because the $\angle$AOB angle of 65° is different from the $\angle$BOC angle of 50° and the length of OA (7.91 nm$^{-1}$) is also different from that of OB (6.06 nm$^{-1}$). In addition, the misfit values of the epitaxial Pd$_2$Si 030 and 002 lattice planes to the Si 220 lattice plane were estimated to be $-7.3$ and $-10.1\%$, respectively, from this TED pattern. On the other hand, the misfit values of bulk-Pd$_2$Si 030 and 002 to bulk-Si 220 are $-2.4$ and $-10.6\%$, and the differences in misfit values between epitaxial and bulk Pd$_2$Si are $-4.9$ and $+0.5\%$ for the 030 and 002 planes, respectively. This result indicates that the hexagonal Pd$_2$Si is formed on the Si substrate with strain, i.e., the a- and c-axes of Pd$_2$Si are tensile- and compressive-strained, respectively.

As mentioned earlier, in the Pd/Si sample, polycrystalline Pd$_2$Si is initially formed at low-temperature agglomerates after additional RTA above 600 °C. On the other hand, in the Pd/Ti/Si sample, a continuous epitaxial Pd$_2$Si layer is uniformly formed after low-temperature annealing. During the subsequent high-temperature RTA, this Pd$_2$Si layer still remains without forming other phases; thus, the agglomeration of the silicide layer hardly occurs owing to the high thermal stability of the epitaxial Pd$_2$Si layers on the Si(001) substrate. As a result, the film morphology of the epitaxial Pd$_2$Si in the Pd/Ti/Si system remains relatively smooth. In the images shown in Figs. 5(b) and 5(c), the flatnesses of the interface are almost similar. These results strongly suggest that the epitaxial growth of Pd$_2$Si layers on Si improves the thermal stability of palladium silicide owing to the low interface energy between silicide and Si compared with the polycrystalline Pd$_2$Si in the Pd/Si system.

As mentioned above, the epitaxially grown Pd$_2$Si with a Ti intermediate layer leads to the high thermal stability of Pd silicide layers in Pd/Ti/Si systems with and without B-doping. Figure 7 shows the sheet resistances of Pd/Ti/Si samples as a function of annealing temperature. Sheet resistance decreases with increasing annealing temperature. This is due to the growth of Pd$_2$Si layers with increasing RTA temperature, as observed in the XRD measurements shown in Fig. 3. The morphological characteristics of the Pd$_2$Si surface in Pd/Ti/Si samples with and without B-doping after annealing at 600 °C are almost similar; thus, the sheet resistances should be similar. However, in this study, the sheet resistance of the Pd$_2$Si layer in the Pd/Ti/Si-undoped sample is similar to that in the Pd/Ti/Si-B-doped sample at 3 × 10^{14} cm$^{-2}$, while that of the B-doped sample at 1 × 10^{15} cm$^{-2}$ is lower than others. We measured the sheet resistance of the substrate prior to loading it into the vacuum chamber. The sheet resistances of the Si substrate for the undoped and B-doped samples at 3 × 10^{14} cm$^{-2}$, and the B-doped sample at 1 × 10^{15} cm$^{-2}$ were about 1000 and 100 Ω/sq, respectively. Therefore, we consider that the sheet resistance of the B-doped sample at 1 × 10^{15} cm$^{-2}$ decreases owing to the parallel conduction of shallow junctions below the silicide layer.

4. Conclusions

We investigated the growth and thermal stability of Pd silicide thin films on heavily B-doped Si(001) using a Ti intermediate layer. Epitaxial or highly oriented Pd$_2$Si in Pd/Ti/Si systems with and without B-doping formed at annealing temperatures of 300–600 °C. The two orientation...
relationships of Pd$_2$Si layers with a Si(001) substrate were Pd$_2$Si[110]∥Si[110] and Pd$_2$Si[110]∥Si[001], and Pd$_2$Si[100]∥Si[110] and Pd$_2$Si[001]∥Si[001]. The agglomeration of Pd$_2$Si in Pd/Ti/Si could be suppressed by the epitaxial growth of Pd$_2$Si at 600 °C with and without heavy B-doping. It seems that the doping of boron atoms on a Si substrate in a Pd/Ti/Si system does not significantly affect epitaxial Pd$_2$Si formation.

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