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REGULAR PAPER

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_2Si was also formed on Pd/Si systems. The agglomeration of Pd_2Si 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_2Si. In addition, epitaxial or highly oriented Pd_2Si formed in Pd/Ti/Si systems. The two orientation relationships of Pd_2Si layers were identified to be $Pd_2Si[1\bar{1}0] \parallel Si[\bar{1}10]$ and $Pd_2Si[110] \parallel Si[001]$, and $Pd_2Si[100] \parallel Si[\bar{1}10]$ and $Pd_2Si[001] \parallel Si[001]$. The formation of strained epitaxial Pd_2Si layers was found in Pd/Ti/Si systems. The improvement in the thermal stability of Pd_2Si and the formation of epitaxial or highly oriented Pd_2Si in Pd/Ti/Si systems were observed with and without B-doping. © 2010 The Japan Society of Applied Physics

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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_2Si,[1] which remains stable up to 700 °C after formation at a low temperature, and the consumption of Si for Pd_2Si formation is smaller than those of NiSi, $NiSi_2$, $CoSi_2$ and $TiSi_2$. In addition, Pd_2Si has a low Schottky barrier height for a p-type contact (~0.3 eV).[2] However, the agglomeration of Pd_2Si 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_2Si 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.[4,5] 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_2Si 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_2Si was completely random.[8,9] It has been reported that epitaxial Pd_2Si 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^{-6} 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) $2\theta/\omega$ 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_2Si 110 and PdSi 211, respectively. These peaks also appear on Pd/Ti/Si samples with

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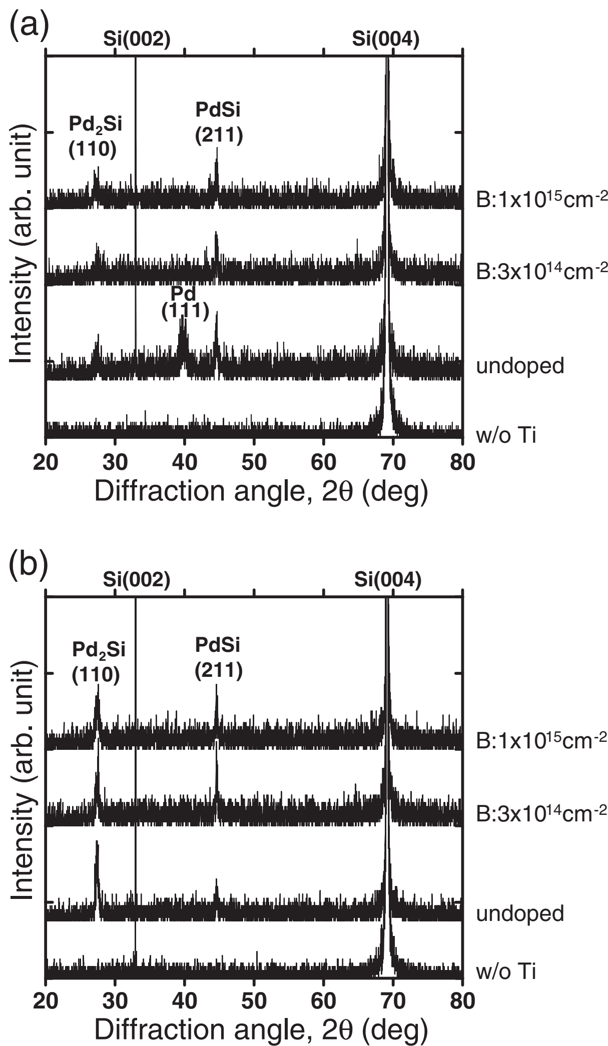

Fig. 1. XRD ($2\theta/\omega$) profiles of the Pd (10 nm)/Si system without Ti interlayer, the Pd (10 nm)/Ti (2 nm)/Si system without B-doping, and the Pd (10 nm)/Ti (2 nm)/Si systems with B-doping at 3×10^{14} cm^{-2} and B-doping at 1×10^{15} cm^{-2} after (a) annealing at 300 °C for 10 min and (b) RTA at 600 °C for 30 s.

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 2θ was used. The grazing-angle XRD 2θ spectra clearly confirmed that polycrystalline Pd_2Si 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_2Si are very weak after annealing at 300 °C. These results indicate the formation of epitaxial or highly oriented Pd_2Si 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_2Si.

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_2Si 110 and PdSi 211 planes. The intensities of Pd_2Si 110 increase with annealing

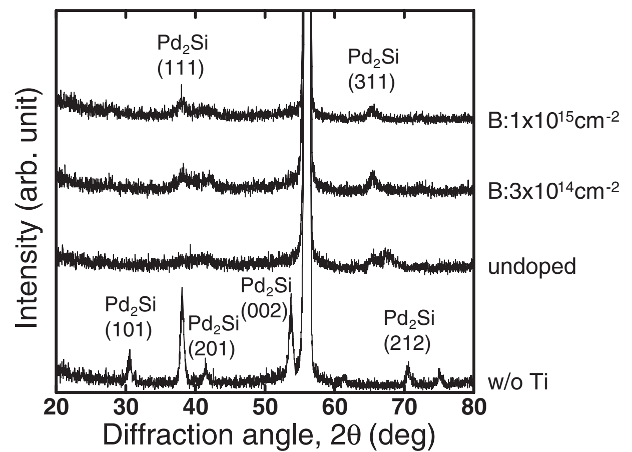

Fig. 2. XRD (2θ) profiles of the Pd (10 nm)/Si systems with and without Ti interlayer, and with and without B-doping at 3×10^{14} and 1×10^{15} cm^{-2} after annealing at 300 °C.

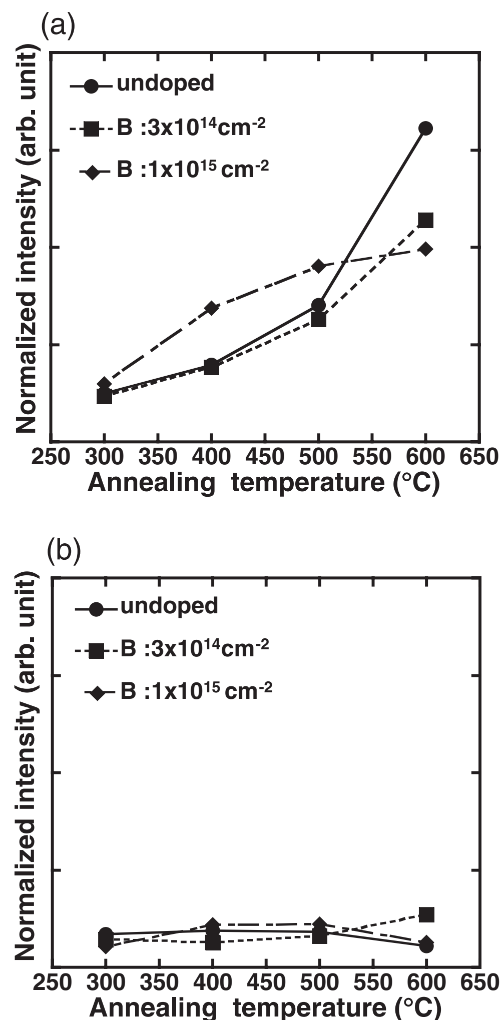

Fig. 3. Normalized intensities of (a) Pd_2Si 110 and (b) PdSi 211 after annealing from 300 to 600 °C in Pd (10 nm)/Ti (2 nm)/Si systems without doping and with B-doping at 3×10^{14} and 1×10^{15} cm^{-2}. Normalized intensity is obtained from all intensities in Fig. 1, which were normalized by the intensity of Si substrates and the powder diffraction intensity ratio of the Pd_2Si 110 and PdSi 211 planes.

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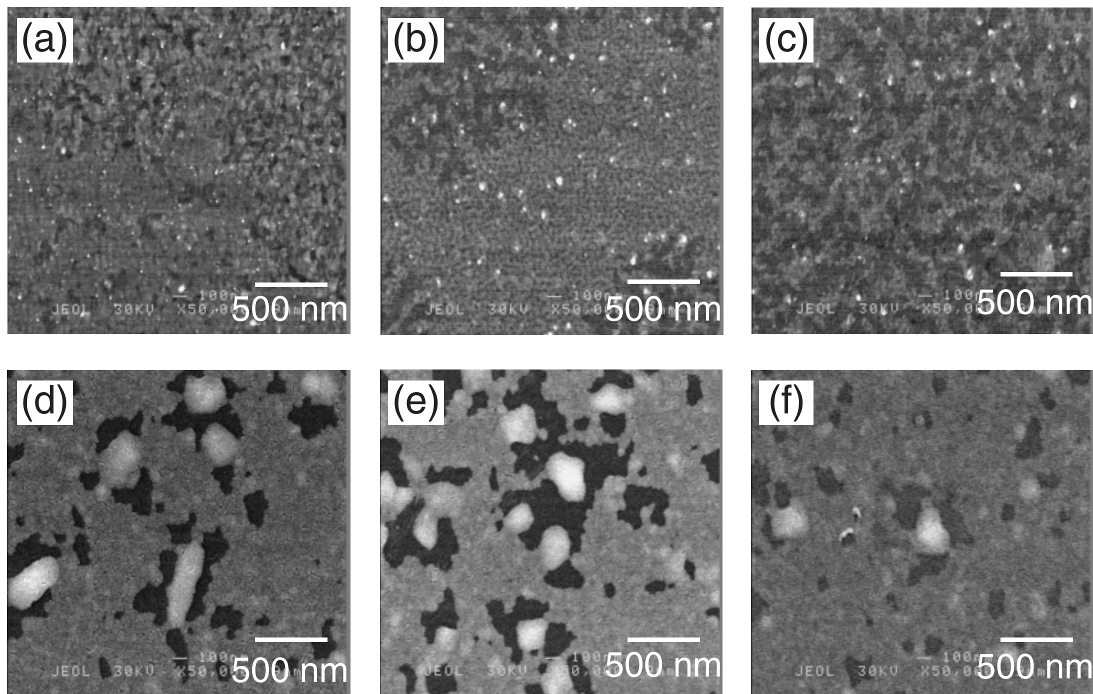

Fig. 4. SEM images of Pd/Ti/Si samples (a) without doping and (b) with B-doping at 3×10^{14} and (c) 1×10^{15} cm^{-2} after RTA at 600 °C for 30 s. Pd/Si samples (d) without doping and (e) with B-doping at 3×10^{14} and (f) 1×10^{15} cm^{-2} after RTA at 600 °C for 30 s.

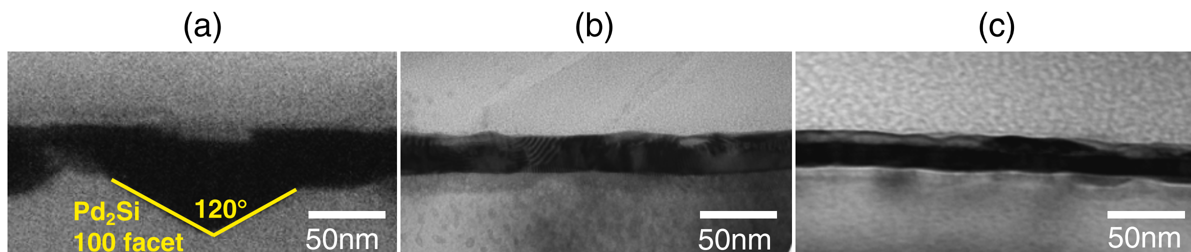

Fig. 5. (Color online) Cross-sectional TEM images of (a) Pd/Si, (b) Pd/Ti/Si-undoped, and (c) Pd/Ti/Si-B-doped 1×10^{15} cm^{-2} samples after RTA at 600 °C for 30 s.

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_2Si domain increases with annealing temperature, while the volume of PdSi domain remains almost constant. These results indicate that Pd_2Si and PdSi are formed during the first-step annealing at 300 °C and we suggest that the growth rate of Pd_2Si 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_2Si 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. Figures 5(a)–5(c) show cross-sectional TEM images of the following samples after annealing at 600 °C: the Pd/Si sample (a), the Pd/Ti/Si sample without doping (b), and the Pd/Ti/Si sample with B-doping at 1×10^{15} cm^{-2} (c). Some polycrystalline Pd_2Si layers 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_2Si 100 planes. On the other hand, the flatnesses of the Pd_2Si/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_2Si, 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_2Si layer on a Si substrate is formed.

Here, we deduced the model of the dependence of interfacial reactions on annealing conditions. In general, Pd_2Si 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_2Si domain rapidly grows. As a result, pyramidal Pd_2Si domains are individually formed with large {100} facets. On the

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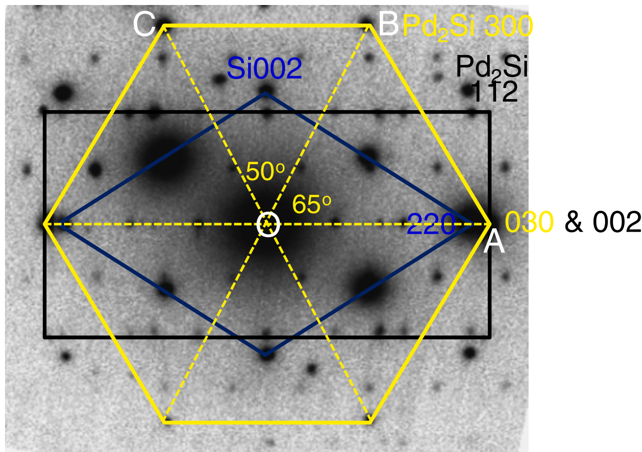

Fig. 6. (Color online) TED of Pd/Ti/Si-undoped sample after RTA at 600 °C for 30 s.

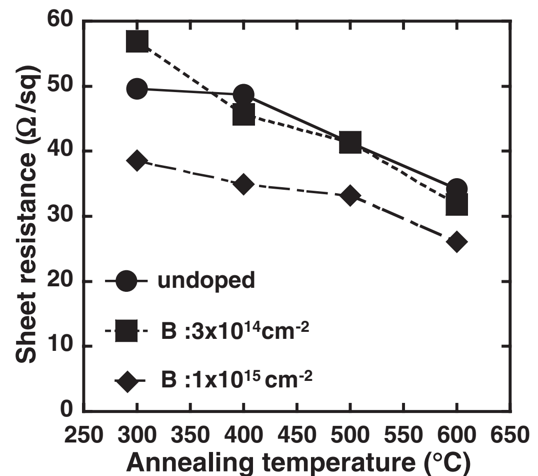

Fig. 7. Sheet resistances of Pd/Ti/Si samples with and without B-doping as a function of annealing temperature.

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_2Si simultaneously and densely occurs. Consequently, the uniform growth of a Pd_2Si 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. This 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_2Si diffraction spots. We observed that Pd_2Si grains are highly oriented with respect to the Si substrate. The epitaxial Pd_2Si structures of the Si substrate were observed from TED patterns. The two orientation relationships of Pd_2Si layers were identified to be $Pd_2Si[1\bar{1}0] \parallel Si[\bar{1}10]$ and $Pd_2Si[110] \parallel Si[001]$, and $Pd_2Si[100] \parallel Si[\bar{1}10]$ and $Pd_2Si[001] \parallel Si[001]$. This result also agrees with the XRD $2\theta/\omega$ spectra of the Pd/Ti/Si system shown in Fig. 1, and this TED observation reveals that epitaxial Pd_2Si 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_2Si 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_2Si 030 and 002 to bulk-Si 220 are −2.4 and −10.6%, and the differences in misfit values between epitaxial and bulk Pd_2Si are −4.9 and +0.5% for the 030 and 002 planes, respectively. This result indicates that the hexagonal Pd_2Si is formed on the Si substrate with strain, i.e., the a- and c-axes of Pd_2Si are tensile- and compressive-strained, respectively.

As mentioned earlier, in the Pd/Si sample, polycrystalline Pd_2Si 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_2Si layer is uniformly formed after low-temperature annealing. During the subsequent high-temperature RTA, this Pd_2Si 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_2Si layers on the Si(001) substrate. As a result, the film morphology of the epitaxial Pd_2Si 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_2Si 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_2Si in the Pd/Si system.

As mentioned above, the epitaxially grown Pd_2Si 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_2Si layers with increasing RTA temperature, as observed in the XRD measurements shown in Fig. 3. The morphological characteristics of the Pd_2Si 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_2Si 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_2Si in Pd/Ti/Si systems with and without B-doping formed at annealing temperatures of 300–600 °C. The two orientation

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relationships of Pd_2Si layers with a Si(001) substrate were $Pd_2Si[1\bar{1}0] \parallel Si[\bar{1}10]$ and $Pd_2Si[110] \parallel Si[001]$, and $Pd_2Si[100] \parallel Si[\bar{1}10]$ and $Pd_2Si[001] \parallel Si[001]$. The agglomeration of Pd_2Si in Pd/Ti/Si could be suppressed by the epitaxial growth of Pd_2Si 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_2Si formation.

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