Epitaxial growth of uniform NiSi2 layers with atomically flat silicide/Si interface by solid-phase reaction in Ni–P/Si(1 0 0) systems

H.F. Hsu a,∗, H.Y. Chan a, T.H. Chen a, H.Y. Wu a, S.L. Cheng b, F.B. Wu c

a Department of Materials Science and Engineering, National Chung Hsing University, Taichung, Taiwan, ROC
b Department of Chemical and Materials Engineering, National Central University, Taoyuan, Taiwan, ROC
c Department of Materials Science and Engineering, National United University, Miao-Li 36003, Taiwan, ROC

A R T I C L E   I N F O

Article history:
Received 15 October 2010
Received in revised form 21 February 2011
Accepted 21 February 2011
Available online 8 April 2011

Keywords:
Nickel silicide
Phosphorous Interface

A B S T R A C T

As metal-oxide-semiconductor field-effect transistor (MOSFET) devices are shrunk to the nanometer scale, flat shallow metal/Si electrical contacts must be formed in the source/drain regions of metal-oxide-semiconductor field-effect transistor (MOSFET) devices. Conventionally, low-resistivity silicides, such as C54–TiSi2, CoSi2 and NiSi, have been used to reduce parasitic resistance. However, these silicides have polycrystalline structures when they form on Si substrates, inhibiting the formation of the atomically flat interfaces that are needed between the silicide layers and Si substrates for the ultrashallow p–n junctions

1. Introduction

As the dimensions of devices are reduced to the nanometer scale, flat shallow metal/Si electrical contacts must be formed in the source/drain regions of metal-oxide-semiconductor field-effect transistor (MOSFET) devices. Conventionally, low-resistivity silicides, such as C54–TiSi2, CoSi2 and NiSi, have been used to reduce parasitic resistance. However, these silicides have polycrystalline structures when they form on Si substrates, inhibiting the formation of the atomically flat interfaces that are needed between the silicide layers and Si substrates for the ultrashallow p–n junctions

The formation of epitaxial silicide on Si substrates has potential for realizing silicide/Si contacts with atomically flat interfaces. The fact that NiSi2 has a small lattice mismatch of −0.4% with Si makes it an attractive material for use in the formation of epitaxial silicide on Si. Epitaxial NiSi2 layers can be easily formed on Si(1 0 0) by annealing Ni films on Si substrates. During the annealing process at a low temperature, Ni-rich silicide phases, such as Ni31Si12 and Ni3Si, form. These can be transformed to the Si-rich silicide phase by further annealing at a high temperature. NiSi2, which is transformed from NiSi, is the final stable Ni-silicide phase. However, the NiSi2 layer on Si(1 0 0) that is formed by the solid-state reaction of Ni with Si often exhibits a very rough NiSi2/Si interface because of the formation of {1 1 1} facets at the interface thereat [2–6].

Okubo [7] indicated that epitaxial NiSi2 was transformed from the agglomerated NiSi layer, and preferentially formed in the vicinity of the agglomerated NiSi grains and the exposed region of Si, causing the formation of the NiSi2 layer with the {1 1 1}-faceted interface. However, if the epitaxial NiSi2 layer forms at low temperature without the formation of the polycrystalline NiSi phase, then agglomeration of silicide layer is difficult because of the high stability of epitaxial NiSi2 on the Si substrate. Thus, techniques for the formation of an epitaxial NiSi2 layer by low-temperature annealing have been intensively investigated [8–11]. For example, an amorphous Ni–Zr interlayer [8] and BF2+ or B+ ion-implanted Si(1 0 0) substrate [9] can be used to reduce the formation temperature of the NiSi2 phase. However, the NiSi2/Si(1 0 0) interface is still rough because of the presence of {1 1 1} facets. Notably, some researchers have reported on the formation of an epitaxial NiSi2 layer with an atomically flat NiSi2/Si interface [10,11]. Their studies have shown that an epitaxial NiSi2 layer can form at low annealing temperature. The use of a Ti interlayer can reduce the rate of diffusion of Ni atoms into the Si [10]. The nucleation energy of NiSi2 can be decreased by using an Si+ ion-implanted Si(1 0 0) substrate [11]. The {1 1 1} facets remained at the NiSi2/Si(1 0 0) interface at low temperature. Interesting, the NiSi2 layer was transformed to a uniform epitaxial NiSi2 layer with an atomically flat NiSi2/Si interface when the samples were further annealed at high temperature.

This study presents a new method for growing an epitaxial NiSi2 layer on an Si(1 0 0) substrate without employing an interlayer between Ni and Si or an ion-implanted substrate. Instead of pure Ni, an Ni alloy is utilized to retard the supply of Ni to the
Si substrate. For this purpose, an amorphous Ni–P alloy film is deposited onto an Si substrate by sputtering. The epitaxial NiSi₂ films can be formed simply through the solid-state reaction in the Ni–P/Si(1 0 0) system. A high-quality ultra-thin epitaxial NiSi₂ thin film on Si(1 0 0) with an atomically flat NiSi₂/Si interface is demonstrated.

2. Experimental procedure

N-type Si(1 0 0) substrates with a resistivity of 1–10 Ω cm were used. The substrates were cleaned using the standard RCA procedure [12] and then dipped in a dilute HF solution before being loaded into the deposition chamber. Ni–P films, 8 nm in thickness, were prepared by sputtering from an Ni–P target. The base pressure of the chamber was below 6.7 \times 10^{-4} \text{ Pa}. The target-to-source distance was 10 cm. The plasma source (Ar gas) was input to the chamber; the resultant working pressure was 4.1 \times 10^{-1} \text{ Pa}. Before deposition, the target was pre-sputtered for 10 min to clean the target surface. The input power for the Ni–P target was fixed at 50 W and the deposition rate was about 0.1 nm/s. After deposition, the P content in the Ni–P film was measured by EDS analysis of the cross-sectional TEM sample and was found to be about 15 wt.%.

For comparison, pure Ni films, 8 nm in thickness, were prepared on Si(1 0 0). Both the as-deposited Ni–P/Si(1 0 0) and Ni/Si(1 0 0) samples were annealed in a rapid thermal annealing apparatus at 400–750 °C for 30 s in a forming gas (Ar:H₂ ratio, 95:5).

The surface morphologies of the silicides were observed using scanning electron microscopy (SEM). Plane-view transmission electron microscopic (TEM) images and selected area diffraction (SAD) patterns were applied to identify the silicide phases. Cross-sectional TEM images were used to study the reaction at the Ni-silicide/Si interfaces. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used to investigate the distribution of the elements throughout the depth of films. SEM was performed using a JEOL JSM 6700F SEM. The TEM observations were made using a JEOL 200CX TEM and a JEOL JEM-3000F TEM that were operated at 120 and 300 keV, respectively. AES and XPS were carried out with a PHI-700 scanning Auger microscope and a PHI 5000 VersaProbe, respectively.

3. Results and discussion

3.1. Phase transformation and morphology of Ni-silicide thin films in Ni/Si(1 0 0) and Ni–P/Si(1 0 0) systems

Fig. 1 plots the sheet resistance data for Ni/Si(1 0 0) and Ni–P/Si(1 0 0) samples after annealing at 400–750 °C. Following annealing at 400 °C, the sheet resistance of the Ni/Si(1 0 0) sample was lower than that of the Ni–P/Si(1 0 0) sample. It was slightly higher after annealing at 500 °C and was much higher after annealing at 600 °C. The sheet resistance of the Ni–P/Si(1 0 0) samples was lower than that of the Ni/Si(1 0 0) samples when the annealing temperature exceeded 500 °C. The sheet resistance was low until the annealing temperature increased to 750 °C. The results show that the low-resistivity window of the Ni–P/Si(1 0 0) samples was wider than that of Ni/Si(1 0 0) samples. The variation in the sheet resistance is thought to be closely correlated with the phase transformation or change in morphology of the films during silicidation. A discussion of the possible reasons for the variation in the sheet resistance follows.

Table 1 presents the phases of Ni silicide that formed at various annealing temperatures. Fig. 4 shows the morphology of Ni/Si(1 0 0) and Ni–P/Si(1 0 0) samples after annealing at 400–750 °C. In the Ni/Si(1 0 0) system, voids of exposed Si were observed after annealing at 500 °C, as shown in Fig. 4(b). Annealing at 600 °C greatly increased their size [Fig. 4(c)]. When the annealing temperature increased to 700 or 750 °C, the irregular voids became faceted [Fig. 4(d) and (e)]. The proportional areas of the exposed Si substrate in the samples that were annealed at 500, 600, 700 and 750 °C were 17%, 35%, 43% and 44% respectively, indicating serious degradation of the Ni-silicide films as the temperature increased. In the Ni–P/Si(1 0 0) system, the Ni-silicide films were continuous until they were annealed at 750 °C. When the annealing temperature increased to 750 °C, the NiSi₂ film started to degrade, as shown in Fig. 4(j).

Based on the above observations, the dramatic increase in sheet resistance upon annealing of Ni/Si(1 0 0) sample above 600 °C is attributed to the severe agglomeration of the silicide layer. Although the use of the Ni–P alloy layer resulted in the formation of the NiSi₂ phase at low temperature (400 °C), it improved the morphological stability of the silicide films. Thus, the Ni-silicide films that formed in the Ni–P/Si(1 0 0) samples had better electrical properties than did those that formed in the Ni/Si(1 0 0) samples, because of the morphological stability of the silicide films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Si(1 0 0)</td>
<td>400 500 600 700 750</td>
</tr>
<tr>
<td>Ni–P/Si(1 0 0)</td>
<td>NiSi(p) NiSi(p) NiSi(p)NiSi₂(e) NiSi₂(e) NiSi₂(e)</td>
</tr>
<tr>
<td>Ni/Si(1 0 0)</td>
<td>NiSi₂(e) NiSi₂(e) NiSi₂(e) NiSi₂(e) NiSi₂(e)</td>
</tr>
<tr>
<td>Ni–P/Si(1 0 0)</td>
<td>NiSi₂(e) NiSi₂(e) NiSi₂(e) NiSi₂(e)</td>
</tr>
</tbody>
</table>

(p) The structure was polycrystalline. (e) The structure was epitaxial.
3.2. Morphology of Ni-silicide thin films interface in Ni–P/Si(1 0 0) system

Fig. 5 shows the AES depth profiles of the Ni–P/Si(1 0 0) samples that were annealed at various temperatures. The P signal peak was found at the region of the surface at an annealing temperature of 400 °C and was difficult to detect in the silicide film. The results indicate that a capping layer was formed on the region of the surface region that contained the elements Ni, Si, P and O. Ni atoms were thus inferred to have diffused into the Si substrate, and to have reacted there with Si atoms to form a silicide layer. The profiles in Fig. 5 also show that the structure of the Ni–P/Si(1 0 0) sample after annealing from 400 to 750 °C was capping-layer/Ni-silicide/Si-substrate, which indicates that such structure formed in this range of temperatures was stable.

However, the analysis of the cross-sectional TEM image revealed that the morphology of silicide/Si interface exhibited a series of changes as the annealing temperature was increased. Fig. 6(a) and (b) shows that after annealing at 400 °C, a continuous epitaxial NiSi2 layer with a (1 1 1) facet interface was observed. The area of the (1 1 1) facet decreased gradually as the annealing temperature increased. These (1 1 1) facets were completely eliminated upon annealing at 700 °C. The NiSi2 layer was transformed to a uniform epitaxial layer with a flat NiSi2/Si interface. This amorphous layer can be identified as Si–Ni–P–O capping layer by AES analysis (Fig. 5).

The phase formation of nickel silicide is well known to depend on the transport of Ni atoms. de Reus [8] and Nakatsuka [10] reported that Ni–Zr and Ti interlayers can be used as diffusion barriers against the diffusion of Ni into Si, and to induce the formation of epitaxial NiSi2 layers at a low temperature of 350 °C. In this study, the limitation on the transport of Ni atoms by the P diffusion barrier caused Si-rich silicide (NiSi2) to form at low temperature.
The formation of a continuous NiSi\textsubscript{2} film with an atomically flat interface at high temperature (700 °C) is discussed. First, the formation of a capping layer caused the silicide film to remain continuous when it was annealed at high temperature. The previous report shows that thinner Ni-silicide films agglomerated faster [13]. The agglomeration of thin films is driven by the minimization of surface and interface energies. However, the agglomeration can only occur if both Ni and Si are mobile. In this study, the epitaxial growth of NiSi\textsubscript{2} films was found even if the annealing temperature was as low as 400 °C. The fastest paths for diffusion in such epitaxial layer are at surface and interface. A capping layer that contained elemental Ni, P, Si and O formed on the surface of the Ni-silicide layers during annealing, which was more efficient at limiting the diffusion of Ni or Si [14]. Thus, the agglomeration is difficult to occur, causing that a continuous NiSi\textsubscript{2} layers remained until the annealing temperature exceeded 750 °C. Second, the change of morphology of silicide/Si interface is caused by the reducing of the total interface energy. An epitaxial thin film can be regarded as a two-dimensional nanostructure whose total interface energy tends to be reduced either by reducing the area of the interface or by forming an interface with low interface energy [15]. In this study, at low temperature (400 °C), the \{111\} interface energy was much lower than the energy of the other interfaces, causing a large number of \{111\} facets to be formed [5,9,10]. The area of the \{111\} facets decreased as the annealing temperature increased, which was also found in the previous reports [10,16]. The difference in the interface energy between the \{111\} and \{100\} interfaces was thus inferred to decrease as the annealing temperatures increased [17]. Thus, the NiSi\textsubscript{2} layer tended to reduce the total interface energy by minimizing the amount of interfaces. Therefore, a flat \{100\} interface was formed at 700 °C.
4. Conclusion

The epitaxial growth of a NiSi$_2$ layer by solid-phase reactions in Ni(8 nm)/Si(100) and Ni–P(8 nm)/Si(100) samples was investigated. The morphological stability of the Ni-silicide layer was enhanced using Ni–P films. P atoms acted as barriers against the diffusion of Ni atoms to form a stable NiSi$_2$ layer at low temperature. The presence of elemental P was found to result in the formation of a stable capping layer with elements Si, Ni and O during annealing. A continuous epitaxial NiSi$_2$ layer with an atomically flat interface was formed by the formation of an Si–Ni–P–O capping layer and a reduction in the total interface area.

Acknowledgement

The research is supported by the Republic of China National Science Council grant no. NSC 98-2221-E-005-093.

References


Fig. 6. Cross-sectional TEM images of the Ni–P/Si(100) samples after annealing at (a) 400, (c) 600 and (d) 700 °C. (b) Atomic-resolution TEM image of the NiSi$_2$/Si interface and the area corresponds to the rectangle in (a). (e) Atomic-resolution TEM image of the NiSi$_2$ film in (d).