In-Situ Rs and Improvement in Thermal Stability of Nickel Silicides Using Different Interlayer Films

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Abstract: Different interlayer films (Mo, Ru, Ta, Ti and Zn) were proposed to reduce sheet resistance (Rs) and improve thermal stability for nickel (Ni) silicide formation. It was found that the Zn and Mo interlayers reduced nickel silicide Rs much more than those by the Ru, Ta and Ti interlayers at 700 °C. The corrosion rates of the Mo, Ru, Ti and Zn interlayers were higher than that of NiSi in H₂SO₄:H₂O₂ = 4:1 at 80 °C. Overall, Zn and Mo were candidates of interlayers for Ni silicide formation due to lower nickel silicide resistivity, high etching selectivity with NiSi and better thermal stability.

Key words: Interlayer, in-situ Rs, NiSi, silicide.

1. Introduction

Metal silicides have been widely used in ultra-large scale integrated (ULSI) circuits to reduce the contact resistance of the source/drain in complementary metal-oxide-semiconductor (CMOS) devices. Currently, the most commonly used silicides are TiSi₂, CoSi₂ and NiSi. For TiSi₂, the transformation from the high resistivity C49 phase to low resistivity C54 phase is nucleation limited [1-3], causing line-width dependence of the sheet resistance for gate-lines narrower than submicrometer dimensions. Therefore, CoSi₂ and NiSi have emerged as the most promising candidates to replace the C54-TiSi₂ phase in self-aligned silicide (salicide) technology.

Although CoSi₂ is used without significant disadvantages, its high Si consumption and junction spiking have limited its applications with regard to deep submicrometer devices [4]. Neither CoSi₂ nor NiSi have the line-width dependence effects that are observed in TiSi₂ [5]. For sub-100 nm silicide technology, TiSi₂ and CoSi₂ are expected to be replaced by NiSi [6]. For 65-nm node CMOS technology, nickel (Ni) silicide is applied for the lower resistance of the gate electrode and to produce diffused single-silicon layers [7, 8].

Ni silicide is suitable for ULSI because it requires a nano-scale thin film and has a number of desirable characteristics, such as low thermal stress due to low temperature fabrication and low silicon consumption characteristics [9]. However, NiSi agglomeration reportedly takes place at temperatures as low as 600 °C, while its phase transformation from NiSi to NiSi₂ occurs at temperatures above 700 °C [4, 10], and those degrade the performance of the associated devices and give rise to some reliability issues. Recent research has shown that NiSi is extremely sensitive to oxygen contamination during silicidation, but this can be suppressed by adding a TiNₓ capping layer [11]. Accordingly, considerable work has been carried out with the aim of enhancing the phase transformation temperature, specifically by extending the stable temperature region of conventional NiSi by adding a third element, such as Ir or Zr [12, 13].

In this study, the effects of different interlayers were investigated, such as Mo, Ru, Ta, Ti or Zn, on the electrical and thermal properties of Ni silicides. The Ni film diffusivity in Si is faster than interlayers (Mo, Ru,
Ta, Ti or Zn), therefore, the Ni atoms could pass through the interlayer to form silicide. Using the interlayer to replace the capping layer (TiNₓ) would be suitable for next-generation CMOS processes. It is shown that the use of an interlayer effectively improves the electrical characteristics, microstructure properties, thermal stability and phase transformation of the samples.

2. Experiment

The substrates were p-type silicon (100) wafers. Following a standard RCA (Radio corporation of America) cleaning process, different 5-nm interlayer films (Mo, Ru, Ta, Ti and Zn) were sputtered onto a silicon wafer and a 25-nm Ni film was deposited onto different interlayers, as shown in Fig. 1a. The sheet resistance (Rs) of the interlayer Ni silicide was measured by an in-situ Rs method, as shown in Fig. 1b. All samples were annealed at temperatures between 50 °C to 700 °C and measured by the in-situ Rs method in an N₂ ambient.

After the rapid thermal annealing (RTA) silicidation process, the interlayers (Mo, Ru, Ta, Ti and Zn) and unreacted nickel film were selectively etched and removed by dipping in H₂SO₄:H₂O₂ = 4:1 and NH₄OH:H₂O₂:H₂O = 1:8:60 at 80 °C and 25 °C, respectively.

The silicide phases that formed were identified using glancing-angle X-ray diffraction (GLXRD). The surface morphology was observed by field-emission scanning electron microscopy (FESEM). The electrochemical experiments were performed using an AutoLab PGST302N potentiostat/galvanostat with the open-circuit potential (OCP) in the measure-only mode. A conventional three-electrode cell setup with a Pt sheet as the counter electrode and silver/silver chloride (Ag/AgCl)(3M KCl) as the reference electrode was employed.

3. Results and Discussion

Fig. 2 shows the in-situ Rs of the silicide layers formed on different metal interlayers with annealing temperatures from 50-700 °C. The silicide of the Ni/Si structure without a metal interlayer had Rs of less than 60 ohmic/sq at temperatures from 50-700 °C. There was a sudden drop in Rs in the 300-400 °C annealing temperature range that was ascribed to the phase transformation from Ni-rich silicides to NiSi because NiSi has the lowest resistivity of the examined materials. When metal interlayers were inserted, the Rs of Ni silicide was lower at annealing temperatures below 400 °C. In contrast the Ni/Si without any interlayer

![Fig. 1 Illustration of experimental procedure: (a) sample process and (b) In-situ Rs method.](image-url)
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showed Rs of about 35 ohmic/sq at annealing temperatures from 300-400 °C. When the Mo, Ru and Zn interlayers were added to the Ni/Si system, there was a rapid drop in the Rs curve at higher temperatures (450-650 °C). When the Mo, Ru and Zn interlayers were added to the Ni/Si system, there was a sheet resistance of 3-10 ohmic/sq at annealing temperatures from 450-650 °C. On the other hand, when the Ta and Ti interlayers were added to Ni/Si, there was a sheet resistance of 12-15 ohmic/sq at annealing temperatures from 450-650 °C. This indicates that the Mo, Ru and Zn interlayers can improve the thermal stability of Ni silicides. Fig. 2 shows that the Zn-inserted nickel silicide had the lowest NiSi formation temperature of 300 °C. Even that, the Rs of the Zn-inserted nickel silicide could sustain at ~2.5 ohmic/sq at annealing temperatures from 300 °C to 600 °C and then slightly rise to ~4.3 ohmic/sq when the annealing temperature was greater than 600 °C. In this study, Zn performed the best NiSi thermal stability among all metal interlayers.

The GLXRD plots of the Ni films with the Mo, Ru, Ta, Ti and Zn interlayers at 500 °C and 700 °C are shown in Figs. 3a and 3b, respectively. Fig. 3a shows that there were NiSi peaks at 2-theta of 30°-60° and no NiSi₂ peaks in the Mo, Ru, Ta, Ti and Zn interlayer samples at annealing temperature of 500 °C. Fig. 3b shows that the low-resistance phase “NiSi” still existed at 700 °C for all samples, but the high-resistance phases “NiSi₂(200)” were formed in the Ta and Ti interlayer Ni silicide. In the Ru interlayer Ni silicide, there was a (NiRu)Six alloy phase at 2 theta of 41°, but this still does not cause an increase in the Rs. In addition, the Zn interlayer nickel silicide which had the lowest Rs at 300-700 °C had higher NiSi(211) and NiSi(310) peaks at the annealing temperature of 500 °C. The result may indicate that the NiSi(211) and NiSi(310) had lower resistance than other NiSi phases.

Fig. 4 shows the FESEM images of the surface condition of Mo, Ru, Ta, Ti and Zn inserted nickel silicide at a silicidation temperature of 500 °C. The Mo, Ru and Zn interlayer nickel silicide shown in Figs. 4a, 4b and 4e has a relatively smooth uniform surface at 600 °C, while the Ta and Ti interlayer layer nickel silicide gradually has disordered surface grains, as shown in Figs. 4c and 4d. The disordered surface grains have an average width of 100-350 nm.

Fig. 5 shows the FESEM images of the surface condition of Mo, Ru, Ta, Ti and Zn inserted nickel silicide at silicidation temperature of 700 °C. In contrast in Figs. 4a, 4b and 4e average grain width is 20-30 nm, in Figs. 5a, 5b and 5c the average grain width is 40-50 nm. The disordered surface grains of Ta and Ti interlayer nickel silicide in Figs. 5c and 5d, show more agglomeration than those in Figs. 4c and 4d.
**Fig. 3** GLXRD plots of the nickel silicide with different interlayers at the annealing temperature of: (a) 500 °C and (b) 700 °C.

**Fig. 4** Plan-view FESEM images of Ni silicides that were obtained from different interlayers (Mo, Ru, Ta, Ti and Zn) and annealed at 600 °C.

Fig. 6 shows the FESEM images of the surface condition of Mo, Ru, Ta, Ti and Zn inserted nickel silicide at a silicidation temperature of 800 °C. Figs. 6a and 6b show evident surface roughness, but in Fig. 6c the Zn interlayer nickel silicide is still effective in inhibiting surface agglomeration. The disordered surface grains of Ta and Ti interlayer nickel silicide shown in Figs. 6c and 6d have a surface roughness higher than those in Figs. 4 and 5. These result show that the Ta and Ti interlayer nickel silicide inhibits surface agglomeration less and has worse thermal stability than Mo, Ru and Zn interlayer nickel silicide. In contrast, the Zn interlayer nickel silicide inhibits the surface agglomeration more and has better thermal stability than the Mo and Ru interlayer nickel silicide.

Fig. 7 shows the TEM images of the cross-sectional of (a) Ni/interlayer before annealing, (b) Ni/Mo/Si, (c) Ni/Ru/Si, (d) Ni/Ta/Si, (e) Ni/Ti/Si and (f) Ni/Zn/Si at 700 °C. In Figs. 7b-7f, the nickel-silicide films were irregular with grooves at the silicide/Si interface. In Figs. 7b and 7f, the nickel-silicide films are still smooth. A signify the Mo and Zn metal inhibit surface
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Fig. 6  Plan-view FESEM images of Ni silicides that were obtained from different interlayers (Mo, Ru, Ta, Ti and Zn) and annealed at 800 °C.

Fig. 7  TEM cross-sectional profiles of (a) Ni/interlayer before annealing, (b) Ni/Ti/Si 700 °C, (c) Ni/Ru/Si 700 °C, (d) Ni/Zn/Si 700 °C, (e) Ni/Ti/Si 700 °C and (f) Ni/Zn/Si 700 °C.

Agglomeration behavior was better than Ru, Ta and Ti. Figs. 7c-7e exhibit Ru, Ta and Ti interlayer annealing at 700 °C. The result found the nickel-silicide films was irregular with grooves and inhibits surface agglomeration less than Mo and Zn metal.

Fig. 8 shows the Tafel corrosion rate curves of NiSi and different metal interlayers (Mo, Ru, Ta, Ti and Zn) in the H$_2$SO$_4$:H$_2$O$_2$ = 4:1 selectivity etching solution at 80 °C. It was seen that the corrosion currents ($I_{corr}$) of the Mo, Ru, Ti and Zn films were higher than that of NiSi while the $I_{corr}$ of the Ta film was lower than that of NiSi.

Table 1 also shows that the etching rates of the NiSi and different metal interlayers in the H$_2$SO$_4$:H$_2$O$_2$ = 4:1
Fig. 8  Potential dynamic curves of the different interlayer (Mo, Ru, Ta, Ti and Zn) in $H_2SO_4:H_2O_2 = 4:1$ selectivity etching solution at 80 °C.

Fig. 9  Potential dynamic curves of the Ni$_2$Si, NiSi and NiSi$_2$ in $H_2SO_4:H_2O_2 = 4:1$ selectivity etching solution at 80 °C.

Table 1  $I_{corr}$ and etching rates of NiSi and different metal interlayers in the $H_2SO_4:H_2O_2 = 4:1$ solution at 80 °C.

<table>
<thead>
<tr>
<th>Interlayer</th>
<th>Mo</th>
<th>Ru</th>
<th>Ta</th>
<th>Ti</th>
<th>Zu</th>
<th>NiSi</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{corr}$ (A)</td>
<td>$2.79 \times 10^{-2}$</td>
<td>$6.31 \times 10^{-2}$</td>
<td>$8.14 \times 10^{-4}$</td>
<td>$8.87 \times 10^{-3}$</td>
<td>$2.54 \times 10^{-2}$</td>
<td>$3.97 \times 10^{-3}$</td>
</tr>
<tr>
<td>Remove rate (nm/min)</td>
<td>2.5</td>
<td>1.3</td>
<td>0.72</td>
<td>0.85</td>
<td>3.3</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The data also proved that the etching rates of Mo, Ru, Ti and Zn were higher than that of NiSi. In self-aligned silicidation process, the metal interlayers should have higher etching rate than that of NiSi in the selective etching solution to remain NiSi.

Fig. 9 shows the Tafel corrosion rate curves of the different nickel-silicide phases (Ni$_2$Si, NiSi and NiSi$_2$) in the $H_2SO_4:H_2O_2 = 4:1$ selectivity etching solution at
80 °C. It is seen that the corrosion currents ($I_{corr}$) of the Ni$_2$Si films are much higher than those of the NiSi and NiSi$_2$ films. However, the Ni$_2$Si-Rs were higher than NiSi-Rs and the NiSi-Rs were lower than NiSi$_2$-Rs. In this work, the corrosion rate of the metal must higher than nickel silicide (NiSi phase). It is found that the corrosion current ($I_{corr}$) of the NiSi films are much lower than that of the Mo, Ru and Zn films in H$_2$SO$_4$:H$_2$O$_2$ = 4:1 selectivity etching solution at 80 °C.

Table 1 shows the metal etching rate in H$_2$SO$_4$:H$_2$O$_2$ = 4:1 at 80 °C and Rs at 700 °C of the different metal interlayers (Mo, Ru, Ta, Ti and Zn). The results prove that the removal rates of the Mo and Zn films are much fast than those of the Ru, Ta and Ti films in H$_2$SO$_4$:H$_2$O$_2$ = 4:1 at 80 °C that the corrosion current ($I_{corr}$) of the Mo and Zn films are lower than those of the Ru, Ta and Ti films at 700 °C.

4. Conclusions

In this study, the effects of different interlayers (Mo, Ru, Ta, Ti and Zn) $in-situ$ Rs on the thermal stability and structural properties of nickel silicide films were investigated. Both without and with an interlayer, the sheet resistance (Rs) increased with increasing annealing temperature, and the interlayers (Mo, Ru, Ta, Ti and Zn) showed better characteristics. The results prove that the Rs of the Ru and Zn films are low than those of the Mo, Ta and Ti films at 700 °C. The GLXRD results show that the Zn interlayer nickel silicide has the lowest sheet resistance of the $in-situ$ Rs at 300-600 °C. The FESEM images show that the Zn interlayer nickel silicide inhibits both surface agglomeration and thermal stability more than the Mo and Ru interlayer nickel silicide. Both Ta and Ti interlayers were not effective in inhibiting surface agglomeration and thermal stability. Because the nickel film which had a diffusion behavior is better than interlayer (Mo, Ru, Ta, Ti or Zn), which choose inhibit diffusion behavior was bad of metal for silicidation. The Tafel corrosion rate shows that the intrinsic corrosion rate of the Mo and Zn films is much higher than that of the Ru, Ta and Ti films, and the metal etching rate of the Mo and Zn films is much faster than that of Ru, Ta and Ti films in H$_2$SO$_4$:H$_2$O$_2$ = 4:1 at 80 °C. It is found that the corrosion current ($I_{corr}$) of the NiSi films are lower than that of the Mo, Ru and Zn films in H$_2$SO$_4$:H$_2$O$_2$ = 4:1 selectivity etching solution at 80 °C. The Ta and Ti interlayer had the best inhibit diffusion behavior, which corrosion rate was lower than Mo, Ru, Zn, and NiSi phase.

References