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Microelectronic Engineering 83 (2006) 345–350
MICROELECTRONIC ENGINEERING
www.elsevier.com/locate/mee

The improvement of thermal stability of nickel silicide by adding a thin Zr interlayer

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Received 25 March 2005; received in revised form 3 October 2005; accepted 3 October 2005
Available online 25 October 2005

Abstract

This is the first report of a technique for inserting a thin Zr interlayer into a nickel film to improve the thermal stability of the silicide formed from this film. The sheet resistance of resulting Ni(Zr)Si film was lower than 2 Ω/□. X-ray diffraction and Raman spectral analysis showed that only the silicides low resistance phase (NiSi), rather than high resistance phase ($NiSi_2$), was present in the sandwich structure. This proves that the incorporation of a thin Zr interlayer into NiSi delayed the occurrence of $NiSi_2$ phase and widened the upper boundary of silicide formation window by about 100 °C. These experimental results could be explained by Gibbs free energy theory. Furthermore, Ni(Zr)Si/Si Schottky diodes were fabricated by rapid thermal annealing at 650, 700, 750 and 800 °C in order to study the *I–V* characteristics of the SBD diodes. The barrier height generally fixed at 0.63 eV, and the ideality factor was close to 1. These results show that Ni(Zr)Si film is a favorable local interconnection and contact silicide material.

Keywords: Ni(Zr)Si; X-ray diffraction; Raman spectral analysis; Rutherford backscattering spectrometry; Schottky barrier diode

1. Introduction

Refractory metal silicide is generally considered as a suitable material for contact formation and for local interconnection. At present, silicides are used widely in very large and ultra large integrated circuits (VLSI/ULSI), because of their low sheet resistivity, self-alignment, and strong tolerance of high temperatures. $TiSi_2$ had been used almost exclusively as salicide material for submicron devices before the introduction of $CoSi_2$ for sub 0.25 μm devices. The need to replace $TiSi_2$ is due to the vital effect of incomplete transformation from the C49 to C54 phase. In view of the large Si consumption, high junction leakage and large stresses associated with $CoSi_2$, nickel silicide has become an attractive candidate material for use in integrated circuits with deep submicron geometries.

Nickel silicide does not seem to exhibit the drawbacks of $TiSi_2$ and $CoSi_2$ [1]. Unfortunately, the thermal stability of NiSi is worse than $TiSi_2$ and $CoSi_2$ and NiSi film agglomeration occurs at temperatures greater than 650 °C and the high resistivity phase $NiSi_2$ nucleates at 750 °C. Recently, many studies have focused on how to delay the transformation from NiSi phase to $NiSi_2$ phase and improve the thermal stability of NiSi.

In the past, it has been demonstrated that inserting either elemental Pt or Pd in the nickel film enhances the thermal stability of nickel silicide [2–5]. This paper provides the first demonstration that a small amount of elemental Zr significantly improves the thermal stability of NiSi. Zr is a cheaper material allowing for some reduction in unit-step cost. In addition, it is possible to use zirconium nitride as a reactive ion-etching mask. This is an added benefit over previous work.

2. Experimental

In this experiment, an epitaxial layer about 9–10 μm with the phosphorus impurity concentration of $5 \times 10^{15}\ cm^{-3}$ was grown on bare silicon ⟨1 1 1⟩ wafers with the arsenic

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0167-9317/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2005.10.001

doping concentration of $1 \times 10^{19}\,cm^{-3}$. Wafers were cleaned with a buffered HF rinse, and then loaded immediately into an S-gun magnetron sputtering system. When the base pressure of the system dropped to 5.2×10^{-5} Pa, the chamber was filled with argon gas until the pressure of the ambient system kept at 10^{-3} Pa, and then the metal sandwich structure of three layers, 30 nm Ni/2 nm Zr/15 nm Ni was sputtered on the epitaxial substrates. After removal from the sputtering system, the films received a first RTA of 600 °C for 40 s in an N_2 ambient to obtain the ternary silicide. After the thermal treatment, the unreacted metal was etched selectively with a mixture of H_2SO_4 and H_2O_2 for several minutes. A second RTA step was carried out at temperatures ranging from 600 to 900 °C for 40 s to complete formation of the ternary compound.

Four point probe (FPP) was used to measure the sheet resistivity of the formed silicide film. Rutherford backscatterring spectrometry (RBS) was employed to estimate Zr atomic ratio in the silicide and the thickness of the silicide film. Its physical phase was identified by both XRD analysis and Raman spectral analysis. The electrical properties of the Ni(Zr)Si/Si Schottky barrier diodes were measured with an HP4156B semiconductor parameter analyzer.

3. Results and discussion

3.1. Sheet resistivity of Ni(Zr)Si film

Sheet resistivities of annealed Ni/Zr/Ni/Si and capped Ti/Ni/Si samples as a function of different temperatures occurring in the second RTA application are shown in Fig. 1. For the Ti/Ni/Si capped structure, sheet resistance of the formed silicide film averaged 3.2 Ω/□ When the capped Ti/Ni/Si sample was heated to 750 °C, its sheet resistance increased up to 4.5 Ω/□ as reported by Zhang et al. [6]. However, the sheet resistance of the Ni(Zr)Si silicide film formed at the RTA temperature from 600 to 800 °C, was lower than that of pure NiSi film, and varied from 1.5 to 1.8 Ω/□. In addition, the Ni(Zr)Si thin film was smooth and bright, and the minute particles in the silicide film were distributed evenly. As soon as the RTA temperature was raised above 850 °C, the sheet resistance of the films raised rapidly. Although it seemed as if the surface of the samples stayed bright and reflective, the silicide interface became roughness and the average grains size of silicide was observed to increase apparently because of the phase transition from low resistance of NiSi to high resistance of $NiSi_2$. The experimental results above demonstrate that adding the Zr interlayer into the nickel film can significantly improve the thermal stability of pure NiSi, and make the transition point of the temperature from NiSi to $NiSi_2$ rise up to at least 800 °C.

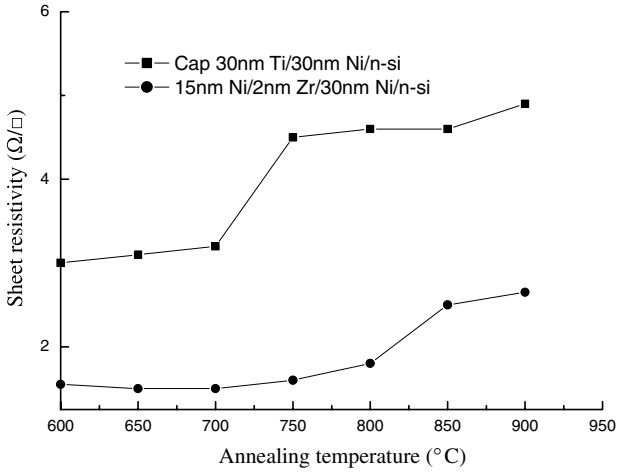

Fig. 1. Sheet resistances of the films with Cap Ti/Ni/Si and Ni/Zr/Ni/Si as a function of RTA temperatures.

3.2. The XRD analysis of the Ni(Zr)Si film

Fig. 2(a) and (b) shows the XRD results of annealed 30 nm Ni/Si and 15 nm Ni/2 nm Zr/30 nm Ni/Si samples as a function of the RTA temperature. For Ni/Si samples, the XRD results for four different samples annealing temperatures are shown in Fig. 2(a). Pure Ni/Si samples annealed at 600 and 700 °C, exhibited monosilicide formation, and (1 1 1)NiSi, (2 0 2)NiSi reflections were observed. When the RTA temperatures were 750 and 800 °C, respectively, the phases of high resistance were detected by X-ray diffraction, as shown by the appearance of (2 0 2)$NiSi_2$ and (4 2 2)$NiSi_2$ reflections. XRD results at three different temperatures are shown in Fig. 2(b) for the Ni/Zr/Ni/Si samples, Ni/Zr/Ni/Si samples annealed at 650 and 800 °C, demonstrate that, besides silicon phases, there existed some NiSi phases, such as (1 1 3)NiSi and (1 1 2)NiSi. The high resistance $NiSi_2$ phases (such as (1 1 3)$NiSi_2$, (4 2 2)$NiSi_2$) were not observed until the RTA temperature was greater than 850 °C. Therefore, the Zr interlayer in the Ni film can postpone phase transformation from NiSi to $NiSi_2$, and elevate the temperature of forming $NiSi_2$ to 800 °C or more.

3.3. Raman spectral analysis of the Ni(Zr)Si film

Raman spectroscopy was employed to investigate the physical orientation of pure NiSi and Ni(Zr)Si silicide, respectively. For pure 30 nm Ni/Si samples, these silicide were formed at different temperatures of 650, 750 and 800 °C, while for 15 nm Ni/2 nm Zr/30 nm Ni/Si the ternary silicide formed at different temperatures of 650, 800 and 850 °C. The Raman spectral experiment was performed with a Renishaw 1000 spectrometer using a 633 nm laser wavelength. Fig. 3(a) and (b) summarizes the Raman analysis for two kinds of samples with pure Ni/Si and Ni/Zr/Si. For Ni/Si samples, all experimental results are shown in Fig. 3(a). There existed two strong peaks of Raman spectral for 30nm Ni/Si annealed at 650 and 750 °C, which were at 215 and 195 cm^{-1}, respectively. The peak located at 215 cm^{-1} results from NiSi [7,8], as did another peak located at 195 cm^{-1} [9]. However, for 30 nm