Extended Abstracts of the 2000 International Conference on Solid State Devices and Materials, Sendai, 2000, pp. 408-409

A-7-5

Effect of Silicon Surface Conditions before Cobalt-Silicidation on Ultra Shallow p^+-n Junction Properties

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1. Introduction

Cobalt di-silicide ($CoSi_2$) is a suitable material to form low-resistance metal-silicon contact, and it is widely used as a the source/drain electrode of high-speed Si-based MOSFETs [1]. The interface between $CoSi_2$ film and a Si substrate is very rough (typical rms-roughness: 5-10 nm). The $CoSi_2$ electrode must be formed on very shallow p^+-n or n^+-p junctions (less than 50-100 nm) in MOSFETs for near future, and the process control of $CoSi_2$ formation is difficult. Surface treatment before Co deposition is a crucial factor, and additional dry-processes such as pre-amorphous-implantation or Ar-sputtering-cleaning complicate the IC process. Wet treatment is appropriate for use in mass-production because it is simple and stable and it has a high throughput. In this paper, a typical roughening mechanism is clarified, and a suppression method is demonstrated based on wet treatment for $CoSi_2$ formation on a p^+-Si(100) surface.

2. Experiment

The substrates used were n-type Si(100) (3-5 Ω·cm), and a 5-nm-thick protective oxide was formed on their surfaces in a dry O_2 ambient at 800°C. Ion implantation then formed a shallow p^+ layer on these surfaces (B^+ 3 ~ 5 keV, 2e15 ~ 5e15/cm^2). Activation annealing was next in a N_2 ambient (1000°C, 10 s). Then the protective oxide that covered the p^+ layer was stripped off by wet treatment before Co deposition. To compare the effects of wet treatment on $CoSi_2$ film properties, three types of fluorine-based solution were examined: a conventional 0.6% HF dip, a BHF (0.2% HF + 35% NH_4F) treatment, and an ammonium-sulphate-added BHF (SBHF) treatment. After wet treatment, a 10-nm-thick Co film was deposited on these surfaces with the sputtering method at room temperature, and the surface was subsequently covered with TiN film. Silicidation annealing was done in a 500 Torr Ar ambient at temperatures in a range of 425 to 730°C.

Transmission electron microscopy (TEM) and X-ray diffraction spectroscopy (XRD) were done on these samples. The $CoSi_2$/Si interface roughness was measured by atomic force microscopy (AFM) after the $CoSi_2$ films were stripped off in 5% HF solution. The electrical leakage of the p^+/n junction was measured under a reverse bias condition for some square-shaped electrodes (80 x 80 ~ 640 x 640 μm^2).

3. Results and Discussion

Table 1 lists AFM-measured interface roughness between $CoSi_x$ and Si substrates. The interface roughness increases steeply during $CoSi_2$ formation, depending on the pre-deposition conditions. Figure 1 compares cross-sectional TEM photographs of TiN/$CoSi_2$/Si(100) structures. The sample prepared with a conventional HF treatment shows a very rough interface, and it has a typical faceted boundary cut into the substrate. The ingrowing near the $CoSi_2$ grain boundary is especially large. These faceted boundaries were always observed at an interface under the grain of $CoSi_2$(100)//Si(100). The samples prepared with BHF or SBHF had less or no $CoSi_2$(100)//Si(100) grains. Figure 2 shows an XRD spectra of $CoSi_2$/p^+-Si(100) samples. We found that two types of diffraction from $CoSi_2$ films strongly depend on pre-deposition conditions. One type is $CoSi_2$(400), which comes from the epitaxially grown grain of $CoSi_2$(100)//Si (100), and the other is the twin grain of $CoSi_2$(211)//Si(211), which shows a structure similar to the well-known twin-poly-Si grain ([110]-rotation (ø=109.5°), (211)-Σ3). These grain structures are illustrated in Fig. 3. No diffraction of $CoSi_2$(400) and very weak diffraction of oriented $CoSi_2$(220) which means a $CoSi_2$(221)//Si(211) growth were observed for the SBHF treatment samples, contrasting with the HF treated samples (see Fig. 2).

The lattice constant of $CoSi_2$ is almost same as that of Si, and $CoSi_2$ can epitaxially grow on either the (111) or (100). Because the stable interface between $CoSi_2$/Si is the (111) or (110), $CoSi_2$(100)//Si(100) has a tendency toward boundary facetting [2, 3]. A higher temperature or longer annealing time or both should enhance the facetting growth, and a more epitaxial grain population would result in a rougher interface. Our AFM results are quite consistent with the crystallographic observation from the TEM images and XRD spectra. The observed depth of the ingrowing facets was 10-20 nm against the 30-nm-thick $CoSi_2$ film (see Fig. 1). This depth is quite large and will cause serious leakage problems in very shallow p^+-n or n^+-p junction.

The nucleation and growth of $CoSi_2$ poly-crystal film is sensitively enhanced by residual oxide on Si substrates [4]. The oxide residence properties on Si substrates depend on the pH and composition of the fluorine-based solution used (see Fig. 4). The crystallographic orientation of $CoSi_2$ can be controlled through pre-treatment. This is an attractive technique for mass production. Figure 5 shows the effect of pre-deposition treatment on the junction leakage of $CoSi_2$/p^+-Si(100)/n-Si(100)$_{sub.}$. The results are consistent with AFM roughnesses and crystallographic observation. Suppression of the epitaxial growth of $CoSi_2$ on Si(100) reduced the junction leakage.

4. Summary

The mechanism of interface roughening between $CoSi_2$ film and a Si(100) surface has been shown. The preferential growth of $CoSi_2$(100) on Si(100) and (211)-Σ3-twin grains results in a rough interface, which consists of the (111) or (110) facets on the (100) substrate. The use of pre-deposition wet treatment strongly affected the crystal orientation of poly $CoSi_2$ film on Si(100). An ammonium-sulphate-added BHF treatment suppressed the preferential growth and interface roughening. This wet treatment also improves the p^+/n junction leakage properties.

References

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Table 1: Measured interface roughness of $CoSi_x/p^+$ Si(100). The silicide-films were stripped off in 5% HF solution, and surface roughnesses of the Si(100) were measured with AFM. The initial thickness of the Co film is 10 nm.

AFM rms-roughness: [nm]

Silicidation temp.	425°C	450°C	630°C	730°C
Silicide phase	Co_2Si, CoSi	CoSi	$CoSi_2$	$CoSi_2$
HF	5.7	6.3	7.9	11.3
BHF	5.1	5.4	7.9	8.0
SBHF	5.5	4.7	7.3	5.9

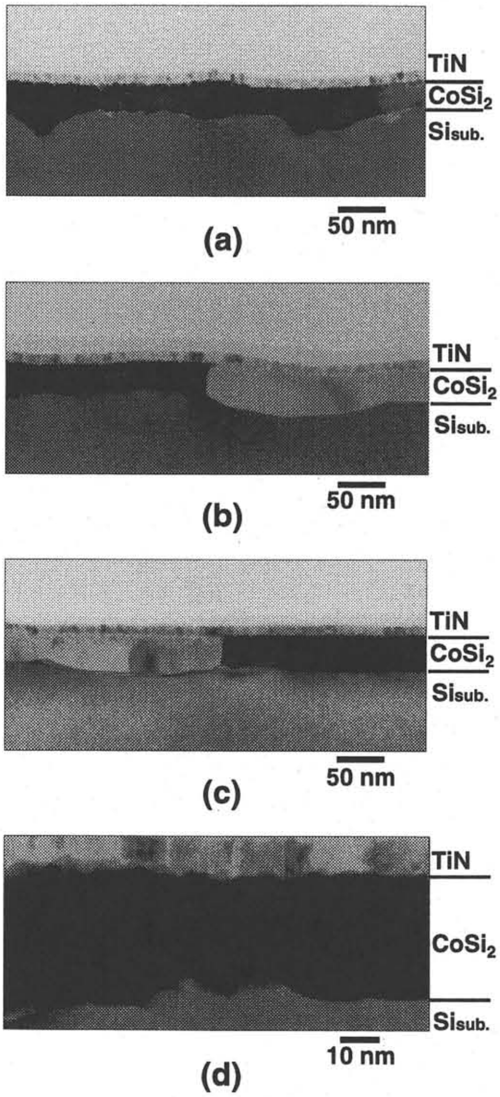

Fig. 1: Cross-sectional TEM photographs of $CoSi_2/p^+$ Si(100). The initial thickness of the TiN and the Co is 10 nm. The substrate is p^+ Si(100) (B^+ 5kV 5e15/cm^2, RTA 1000°C, 10 s). Pre-deposition wet-treatment solutions are (a) 0.6 % HF, (b) BHF, and (c) ammonium-sulphate-added BHF. A typical magnified image of the faceting grain of $CoSi_2$(100)//Si(100) is shown in (d).

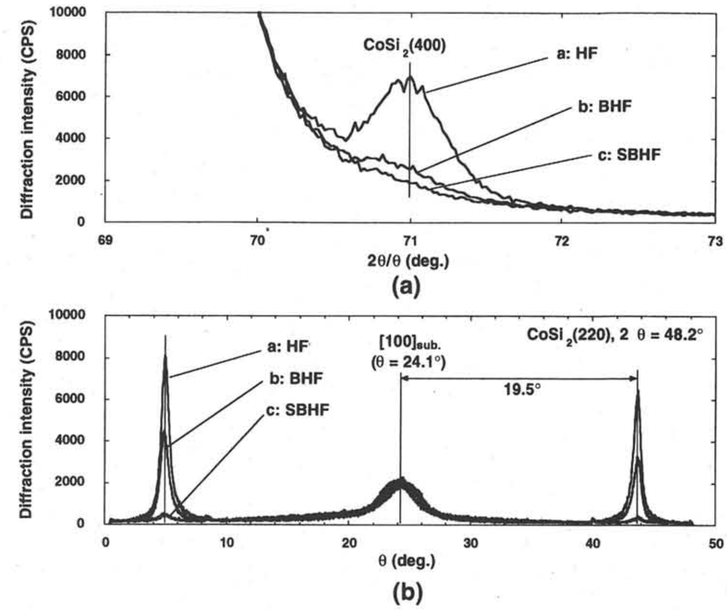

Fig. 2: XRD spectra of $CoSi_2/p^+$ Si(100). Two types of highly oriented grain were found, and these were strongly affected by wet treatment before Co deposition: (a) 2θ/θ diffraction of $CoSi_2$(400) indicating that the relative population of $CoSi_2$(100)//Si(100) depends on pretreatment; (b) the rocking curve of $CoSi_2$(220) in the $(0\bar{1}\bar{1})_{sub.}$ plane. Sharp diffractions of $CoSi_2$(220) were observed at a 19.5° inclined position from the $[100]_{sub.}$.

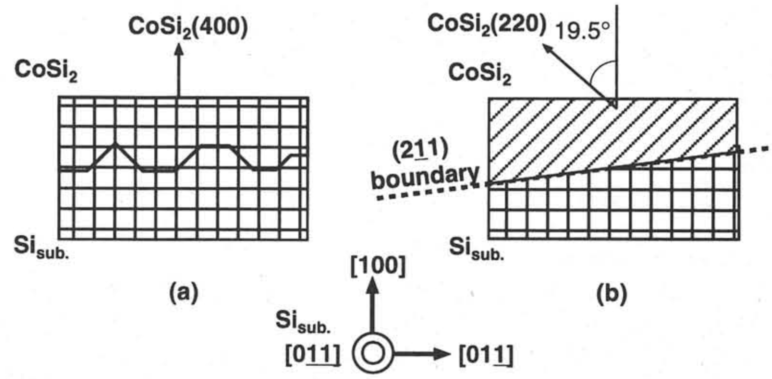

Fig. 3: Epitaxially grown grain models determined from TEM and XRD results: (a) $CoSi_2$(100)//Si(100) model; (b) (211)-Σ3-twin model

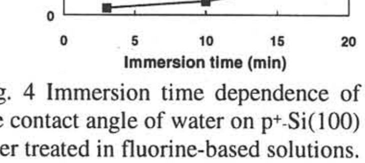

Fig. 4 Immersion time dependence of the contact angle of water on p^+-Si(100) after treated in fluorine-based solutions. The samples were initially covered with 5-nm-thick thermally grown oxide. SBHF effectively reduce residual oxide on p^+-Si(100)

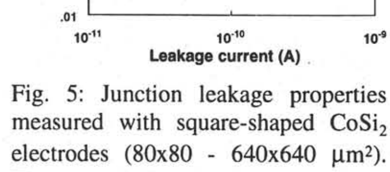

Fig. 5: Junction leakage properties measured with square-shaped $CoSi_2$ electrodes (80x80 - 640x640 μm^2). The very shallow implantation of B^+ 3kV: junction leakage depended on wet pre-treatment, and SBHF effectively reduced leakage current.