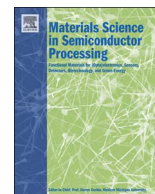




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## Ni and Ti silicide oxidation for CMOS applications investigated by XRD, XPS and FPP

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## ABSTRACT

Although silicide oxidation was studied 20 years ago, the interest of obtaining a robust process for new application appears significant today. Indeed, for the new architectural development process are required dense and narrow spaces. This paper focuses to bury a silicide layer under a protective layer such as silica in order to keep constant the physical and electrical properties of silicide after oxidation. Earlier works show the possibility to oxidize preferably the silicon (Si) in metal contained silicide rather than a pure crystalline Si at high temperatures. Thus, we first tried to reproduce and study these conditions and once acquired, targeted to decrease the oxidation temperature in order to fit with industrial requirements. Titanium (Ti) and Nickel (Ni) are chosen for their metallurgical interest and their integration capability in devices. Thus, four different group/phases (TiSi, TiSi<sub>2</sub>, Ni<sub>2</sub>Si, NiSi) of silicide were targeted by adjusting the temperature. In situ X-ray diffraction (XRD), photoelectron spectroscopy and sheet resistance (four point probe) measurements were carried out simultaneously before and after oxidation of silicide to characterize the phase and chemical composition. After silicide formation last three phases (TiSi<sub>2</sub>, Ni<sub>2</sub>Si, NiSi) were confirmed by XRD and G1(Ti/Si) was unknown, where only for NiSi was observed the low sheet resistance ( $\approx 7.3 \Omega/\square$ ) and resistivity ( $18 \mu\Omega\cdot\text{cm}$ ). After (dry, wet and plasma) oxidation, the phases of TiSi<sub>2</sub> and Ni<sub>2</sub>Si changed and only NiSi was observed the constant phase, even pure SiO<sub>2</sub> was noted on NiSi after wet oxidation.

## 1. Introduction

To increase device functionalities; transistor size decreases and the contact resistance between Si and tungsten(W) plug represents one of the main contributions in series resistance [1,2]. In order to minimize the contact resistance between Si and W plug, a silicide layer is inserted at plug/Si interface. Silicide allows to reduce both contact resistivity and sheet resistance [3–10] and it is also used to fabricate Li ion battery [11]. Silicide is low cost and environment friendly materials and emerging architecture requires new processes where it must be capped by a protective and sacrificial layer. Thus, a well-controlled and protective silica layer can be grown at different oxidation techniques. And it is important to evaluate the oxidation impact on physical and chemical properties of silicide: phase, texture and chemical composition [12]. Due to metallurgical and electrical properties of metal silicide offered different advantages, e.g., capability of oxidizing preferably the silicon rather than the metal [12–14]. Thus, the development technique for covering the metal silicide with an oxide can effect big advantages and numerous applications [13,15]. Detailed, silicide oxidation

procedure is given [13,15–17]. A. Cros et al. [14] observed that during Ni and Pt silicide oxidation both metal and Si atoms are oxidized (Ni<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> formed together) at Ni<sub>3</sub>Si and Ni<sub>80</sub>Si<sub>20</sub> oxidation. But the Ni oxide disappeared beyond annealing at 300 °C and formed SiO<sub>2</sub> and this is a question of free energy formation. Below 800 °C wet oxidation of TiSi<sub>2</sub>, titanium oxide is formed free of silicon, where above 900 °C pure SiO<sub>2</sub> is observed [17,18]. This is due to a kinetics competition between Si oxide and Ti oxide. Dry and wet oxidation of silicide also leads to different oxidation behaviours, Indeed, different authors [12,17,18] reported that silicide oxidation in wet atmosphere presents numerous advantages compared to dry ones: smoother and metal free oxide layer; higher kinetics and reproducible process. In case of dry oxidation, some contradictory results were found. For example, while articles [12,17] reported oxidation of WSi<sub>2</sub> and TaSi<sub>2</sub>, article [13] hardly observed any oxidation. Some authors argued that the metal silicide oxidation rate does not depend on (i) silicide thickness and crystallinity of Si and the (ii) preparation method of silicides [12]. But the oxidation rate are varies because of the crystallinity of Si [15]. M. Bartur et al. [13] strongly argued that the oxidation depends on silicide preparation

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**Table 1**  
Silicidation condition of studied samples.

Sample Name	Metal/ Substrate	Thickness [nm]	Silicidation time [s]	Silicidation temperature [°C]
G1	Titanium	10	60	500
G2	Titanium	10	60	720
G3	Nickel	10	60	300
G4	Nickel	10	60	450

technique. A. Cros et al. [14] observed that the oxidation depends on silicide stoichiometry; the larger the metal content in silicide the easier the oxidation. It has also been reported that SiO<sub>2</sub> growth is much higher on silicide ( $\approx$  double) than on pure silicon [14,17,18], because, metallic bonds in silicide are weaker than the covalent bonds in pure crystalline silicon. We present here the certain oxidation (dry, wet and plasma) conditions to form a protective silica layer on top of the silicide compatible with industrial specifications and keep constant the silicide properties.

## 2. Experimental procedure

After cleaning the samples (200 mm single crystal silicon wafer) in diluted HF solution, were loaded in physical vapour deposition (PVD) tools. Then 10 nm of metal (Ni or Ti) was deposited at 7 Å/s in vacuum maintained at  $5 \times 10^{-7}$  Torr while the emission current set at 50 mA. Both metals were “in situ” capped by TiN layer to prevent from contamination during heat treatment. After completing the deposition process of metal bilayer on silicon substrate, solid state reactions were initiated in RTP850 tools into vacuum atmosphere in order to form Ti and Ni silicides. Thus, different metal phases in Table 1 were targeted applying four annealing temperatures. Temperatures are higher in case of Ti silicide since Ti is more refractory compared to Ni. After silicide formation TiN capping was selectively removed in hot “Caro” solution (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O) and four types of sample consisting of Ti and Ni were obtained.

By introducing the dry oxidizing agent (O<sub>2</sub>) in process tube, oxidation got completed for all the silicides at 300 °C (5 h), 400 °C (5 h), 500 °C (5 h, 10 h and 16 h) and 800 °C (5 h) respectively. Secondly, by introducing steam oxidizing agent (H<sub>2</sub>O) at 800 °C (2 h 30 min, 5 h) oxidation got completed. The ramp up and ramp down rate (10 °C/min and 6 °C/min) were same as dry and wet oxidation. Finally, microwave plasma oxidation was performed (by introducing 90% oxygen and 10% Nitrogen) only for NiSi at 250 °C (5 min) and 300 °C (5 min) respectively. During this oxidation, pressure was kept at 1.5 Torr and operating power at 1500 W. XRD and FPP were used to determine the phase, grain size and sheet resistance (R<sub>s</sub>) of silicide. Copper Cu ( $K\alpha_1$  and  $K\alpha_2$ ) sources employed to perform the experiment at parallel rays model. The grazing incidence angle was set at 2°, scan rate was 0.15°/step while  $2\theta$  was scanned from 20° to 110°. To measure the chemical composition the sample loaded on the sample holder, 8.5 in. inside from the edge of wafer in the XPS chamber. Vacuum was kept at  $1.6 \times 10^{-8}$  Torr and a monochromatic (1486.6 eV Al K<sub>α</sub>) source illuminated the sample with 45° incident angle. For scan mode of analysis, pass energy was fixed at 20 eV and dwell time was 50 ms. Lens mode was fixed in large area and the energy range selected from 0 to 1200 eV during operation. Finally, thermo advantage software was used to analyze the chemical composition and electronic configuration for both silicides and oxides. To identify the elements from the spectra, help was taken from spin orbital splitting and peak area ratios [19].

## 3. Results

### 3.1. Phase determination of silicide before oxidation

After removing the TiN capping the silicides could be directly

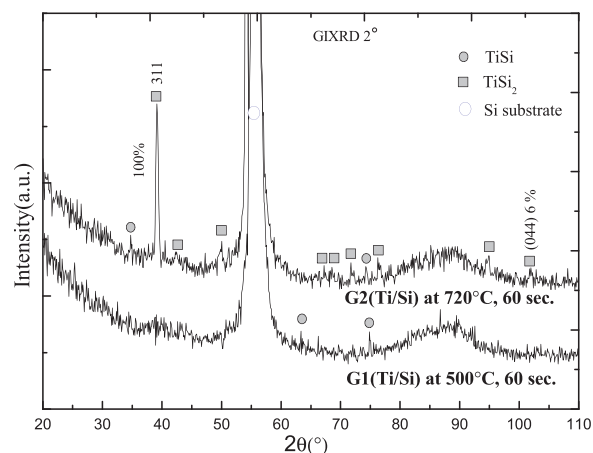


Fig. 1. GIXRD analysis of 10 nm Ti on silicon after 60 s annealing at 500 °C and 720 °C.

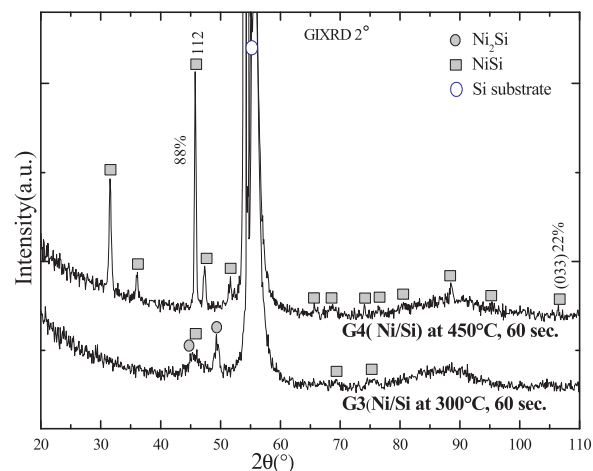


Fig. 2. GIXRD analysis of 10 nm Ni on silicon after 60 s annealing at 300 °C and 450 °C.

analyzed in Figs. 1 and 2, were reported Ti and Ni grazing incidence XRD diagrams. In case of Ti layer annealed at 500 °C (G1), no peak was observed in Fig. 1, bottom spectra. This means that layer can be amorphous or highly textured. Two tiny crystalline peaks were observed and proper matched with TiSi, but these were not enough to identify the phase. After 720 °C (G2), one could observe several peaks with the dominant one at angle 39.10°, Fig. 1, top spectra. Comparing the theoretical values with ten other crystalline peaks, group (G2) was identified as TiSi<sub>2</sub>. Some TiSi grains were observed, but these were probably residues from the transformation of TiSi in TiSi<sub>2</sub>. For Ni/Si system, after 300 °C (G3) two Ni silicide phases coexisted: Ni rich silicide (Ni<sub>2</sub>Si) in particular and Ni mono silicide (NiSi) in Fig. 2, bottom spectra. It seems that at 300 °C during 60 s, Ni<sub>2</sub>Si grew and started to be consumed to the benefit of NiSi. When annealing temperature was higher, 450 °C (G4) directly obtained NiSi in Fig. 2, top spectra. So, Ni silicide was identified as two phases G3(Ni<sub>2</sub>Si) and G4(NiSi).

#### 3.1.1. Phase determination after (dry, wet and plasma) oxidation

G1(Ti/Si) was not considered for oxidation, since it was an unknown phase. After 500 °C (10 h) dry oxidation G2(TiSi<sub>2</sub>) was observed in Fig. 3, the phase was unknown (enough crystalline peaks did not appear). Similarly, Ni<sub>2</sub>Si also changed the phase and formed NiSi at 500 °C (10 h) dry oxidation. Only the phase NiSi was constant in Fig. 4 at dry oxidation. Since the phases TiSi<sub>2</sub> and Ni<sub>2</sub>Si changed at 500 °C (10 h) dry oxidation and were not considered for furnace lowest wet oxidation temperature (800 °C). Only NiSi was oxidized at 800 °C (2 h 30 min and 5 h) and the phase was constant in Fig. 4. Also, in the same figure it was observed that NiSi phase was constant after microwave

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