



Kinetics of growth and consumption of Ni rich phases



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ABSTRACT

In situ X-ray diffraction measurements performed during isothermal annealing show that the life time of θ -Ni₂Si depends on the initial Ni thickness. A slow kinetic of consumption of θ -Ni₂Si is observed during the reaction of 50 nm Ni with Si substrate, while a fast rate of consumption of θ -Ni₂Si is observed when θ -Ni₂Si is a transient phase. The kinetics of growth and consumption of Ni-rich phases is discussed.

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1. Introduction

In advanced integrated circuits, NiSi is the best suited silicide to form ohmic contacts. The introduction of NiSi via the Salicide process allows reducing source, drain and gate resistance built on very thin Si layers for 90 nm technology [1]. In this application, two rapid thermal annealing are used; the first RTA is performed at low temperature to form Ni-rich phases, followed by selective etching of unreacted Ni and subsequent second RTA, at higher temperature, to form the NiSi phase. The fabrication of continuously smaller devices below 90 nm requires the understanding and solution of several material issues that impact the applicability of NiSi. Such issues are the excessive silicidation which is more pronounced for small features, the thermal degradation mechanisms and the growth kinetics of Ni rich phases which precede the formation of NiSi.

In early investigations on the Ni/Si system, the formation of NiSi was found to be preceded by only Ni₂Si phase. However, recent studies, using accurate techniques, revealed a complex Ni-rich phase sequence involving different reacting interfaces [2–4] by the formation of additional Ni-rich phases (Ni₃Si₂, Ni₃₁Si₁₂, Ni₃Si) [4]. The selection of the formation phase depends on the initial Ni thickness and annealing conditions [4]. In addition to the formation of these stable Ni-rich phases, the formation of the metastable θ -Ni₂Si phase; [5,6] has been evidenced in various conditions of preparation. It forms at low temperatures at the θ -Ni₂Si/Si interface and exists during different stages of the formation sequence depending on the initial Ni thickness [7]. The study of the effect

of the initial Ni thickness on the formation phases is also of fundamental and applied interest since it can influence the reaction scheme by controlling the phase sequence formation [8].

The low activation energy that promotes the formation of the metastable θ -Ni₂Si phase over the other stable phases has been explained by the fact that θ -Ni₂Si inherits its texture from θ -Ni₂Si and by the fact that the non stoichiometric θ -Ni₂Si phase forms in strong concentration gradients present at the interface [5,6].

Owing to their technological interest, the kinetics of metal silicides have been investigated in large number of studies: (Ni₂Si) [9,10] (Cobalt, Platinum and Nickel silicides [11], (Ni₃Si₂ [12,13] Ni₃₁Si₁₂ [12]) and (CoSi₂) [14]. Little information about the θ -Ni₂Si phase is available in the literature. It has been shown that, in accordance with simulation, experimental investigations have reported that the growth of θ -Ni₂Si is controlled by nucleation and lateral growth, with a growth rate of $10 \exp(-0.85 \text{ eV/KT}) \text{ cm/s}$ [15].

Hence, more information is still required on the Ni-rich phases especially on the metastable θ -Ni₂Si phase. Indeed, this phase presents some technological interest since it substitutes for θ -Ni₂Si as the first phase during the reaction between Si and the Ni(10% Pt) alloy actually used in microelectronics. It has been reported, that the reaction of a very thin Ni film with a Si(100) substrate leads to the formation of a mixture of NiSi₂ and a θ -Ni₂Si layer exhibiting high thermal stability up to 800 °C [16]. In addition, θ -Ni₂Si may cause high compressive stress annealing [17–19]. Using atom probe tomography, Hoummada et al. [20] have observed the presence of As-rich clusters in the θ -Ni₂Si when the silicidation is performed on an As doped Si substrate allowing a high degree of roughness at the silicide/Si interface. The formation of such clusters at the reaction interface might degrade the device performances.

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Finally, the presence of θ -Ni₂Si has been observed in several conditions regardless of Ni thickness [7], dopants [20], crystalline orientation of the substrates [6] and alloying elements [21]. On the other hand, from kinetic and thermodynamic studies, one can underline the complex consumption mechanism of the θ -Ni₂Si phase and its impact on the formation of the stable phases (θ -Ni₂Si and NiSi). Therefore, data on the kinetics of the formation and the consumption of θ -Ni₂Si in thin films are required.

In this paper, we investigate the effect of Ni initial thickness on the consumption kinetics of θ -Ni₂Si; a kinetic is discussed from the experimental observations.

2. Experiment

Nickel films of 50 and 150 nm in thickness were deposited by sputtering on Si(100) and Si(100) implanted with B substrates. B dopants were implanted with a 2×10^{15} atom cm⁻² dose at 50 keV. In order to activate dopants and to restore the implanted damages, a rapid thermal annealing was subsequently performed at 1080 °C for 2 s.

The Si substrates were cleaned in dilute HF prior loading into the sputtering chamber. The deposition was performed with a base pressure of $\sim 10^{-8}$ Torr using 99.9999% pure Ar gas flow and a 99.99% pure Ni target. To follow the reaction between Ni and Si substrates, samples were analysed by in situ XRD during an isotherm heat treatment at 180 °C. A ramp of 30 °C/min was applied to reach the target temperature. In situ isochronal measurements were also performed. A temperature of 120 °C was first reached with a ramp of 30 °C/min, and then XRD measurements were performed at constant temperature every 5 °C during steps of 1–2 min separated by ramps of 10 °C/min under high vacuum of 10^{-6} Torr to prevent the oxidation of samples.

XRD measurements were performed in the Bragg–Brentano geometry, using a CuK α source and a rapid detector (PANalytical X'Ceerator).

3. Results

Fig. 1 shows the isothermal XRD measurement between $2\theta = 30^\circ$ and 60° at 180 °C realised during the reaction of 50 nm Ni on Si(100) (a), Si(B⁺) (c) and 150 nm Ni on Si(100) (b), Si(B⁺)(d).

The four XRD diagrams show the appearance of the same peaks; they follow different phase sequences depending on the initial Ni thickness and not on the presence of dopants. The peaks at 45° and 48° correspond to the θ -Ni₂Si phase, while the 44° peak corresponds to the Ni film. The peaks corresponding to the NiSi phases, at 47° and 56° , rise in intensity when the Ni film is fully consumed. In this 2θ window, the θ -Ni₂Si phase is characterized by one XRD peak at 47° . Fig. 1 clearly shows that, for the both type of substrates, the consumption of θ -Ni₂Si depends on the initial Ni thickness: for 150 nm Ni, θ -Ni₂Si grows and is consumed in the presence of the Ni film. In the case of 50 nm Ni, θ -Ni₂Si starts to be consumed when the Ni is fully consumed.

The same results have been obtained during isochronal annealing performed during the reaction of 50 and 150 nm Ni with Si(100) and Si(B⁺) (see Fig. 2). Fig. 2 clearly shows that, for the both thicknesses and the both substrates, the XRD peak of θ -Ni₂Si shifts to high angles and then to low angles. This behaviour was also mentioned by Van Bockstael et al. [22] during the reaction of Ni(*x*%Si) with Si(100), $x = 43$ –47% and Mangelinck et al. [15] in the case of 60 nm Ni/Si(100). It is important to notice that in the case of 50 nm Ni, the XRD peak corresponding to θ -Ni₂Si also shifts to high angles when the Ni film is fully consumed (see Fig. 2a and c). This last shift was explained by the relaxation of stress when the growth of θ -Ni₂Si has stopped.

In order to observe the effect of the initial Ni thickness on the kinetics of growth and consumption of the formation phases, we plot in Fig. 3 the normalized area of the peaks corresponding to Ni, θ -Ni₂Si and δ -Ni₂Si versus annealing time at 180 °C for (a and c) 50 nm, (b and d) 150 nm Ni on Si(100) and Si(B⁺) respectively. The area of the XRD peaks should be representative of the volume fraction of these phases. More precisely, the XRD intensity should be proportional to the number of diffracting lattice planes if the crystallinity and the texture do evolve too much. In the case of none stoichiometric phases such as θ -Ni₂Si, The structure factor can also change. The main difference can be observed in this figure is, for both Ni thicknesses, the θ -Ni₂Si phase grows with fast kinetics; while its kinetics of consumption depends on the initial Ni thickness. It vanishes after 2 h and 5 h annealing with 150 nm Ni on Si(100) and Si(B⁺) respectively, while its consumption is delayed to 10 h and 30 h annealing in the case of 50 nm Ni on Si(100) and Si(B⁺) respectively.

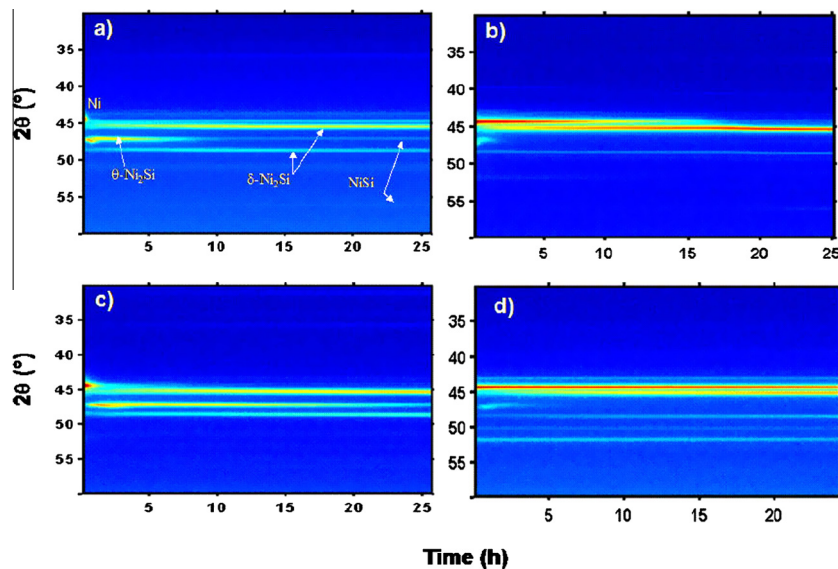


Fig. 1. In situ XRD measurements during isothermal annealing at 180 °C of 50 nm Ni on Si(100) (a), Si(B⁺) (c) and 150 nm Ni on Si(100) (b), Si(B⁺)(d).

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