Formation by nonlinear reactive diffusion of the amorphous Ni silicide upon rapid thermal anneals

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Silicides are used in microelectronics devices as contacts and for technology nodes below 65 nm, the Ni silicide is the preferred material because of its low resistivity as well as the low thermal budget and low Si consumption [1]. Pt has been added to the Ni silicide to limit the detrimental agglomeration issue that becomes more stringent when the silicide thickness is decreased to follow the devices downscaling in microelectronics. The addition fo Pt changes the silicide formation but the kinetics and mechanisms related to these changes have not been deeply investigated. In particular, the kinetics of formation of the first silicide is of great importance when a partial silicidation is performed during the silicide process since it allows to precisely control the final thickness of the contact. Indeed, in the self-aligned silicide process (salicide) with partial silicidation, a given thickness of first silicide is formed during the first rapid thermal anneal (RTA) by selecting the thermal budget and, after selective etch of the unreacted metal, is converted in NiSi with the desired thickness during the second rapid thermal anneal. In this work, the growth kinetics of the first silicide is investigated in detail and a new model considering nonlinear diffusion is proposed for the growth law. The influence of a pre-amorphization implant (PAI) on the first phase kinetics is also investigated.

10 nm $Ni_{0.9}Pt_{0.1}$ layers covered by 7 nm thick TiN capping layer were deposited without vacuum breaking by magnetron sputtering after the substrate cleaning. Rapid thermal anneals (RTA) for five different times at temperatures ranging from 200 to 230°C were then performed in order to keep the reaction partial. The unreacted NiPt and TiN layers were finally removed by wet selective etching for the determination of the silicide thickness by X-ray reflectivity (XRR) with a precision of ± 0.1 nm. TEM analysis coupled with EDX (Electron Dispersive X-Ray) spectroscopy were also performed.

TEM analysis show that the first silicide is an amorphous silicide with a composition ranging between 33 and 45 at.% of Si. A TTT diagram is used to point out the influence of the RTAs on the growth of the amorphous silicide by inhibition of the silicide's crystallization.
The growth kinetics of this amorphous silicide during RTA type annealing was determined by XRR measurements of the silicide thickness (Fig. 1). To determine the growth law, the linear parabolic model is first considered but non-physical parameters were obtained for all samples and all temperatures (Fig. 2). A nonlinear reactive diffusion model in which the growth rate is proportional to the hyperbolic sinus of the gradient of chemical potential is developed to accurately reproduce the experimental results (Fig. 3). This behaviour is attributed to the nanometric thicknesses (< 18 nm) of the amorphous silicide that lead to strong gradient of driving force (chemical potential).
From this model, the effective diffusion coefficient as well as its activation energy were determined for the three samples with PAI and the reference sample without PAI. The differences in effective diffusion coefficients (and activation energy) provide some understanding of the PAI influence on the growth kinetics of the silicidation process. The influence of the substrate amorphization on the silicide growth is discussed : the Ge PAI has an accelerating effect on the silicide formation that could be related to thermodynamic (driving force) but also kinetics (self-diffusion coefficient). However, the Ge+C PAI seems to cancel the influence of the Ge PAI. The validity and applicability of the nonlinear reactive diffusion, considering the application for microelectronics contacts, are also discussed.

References

1. D. Mangelinck, Chap. 9 - Growth of Silicides and Germanides, Handbook of Solid State Diffusion, Elsevier, 2017.
2. C. Delwail, K. Dabertrand, S. Joblot, F. Mazen, D. Mangelinck, Acta Materialia. 262 (2024) 119430

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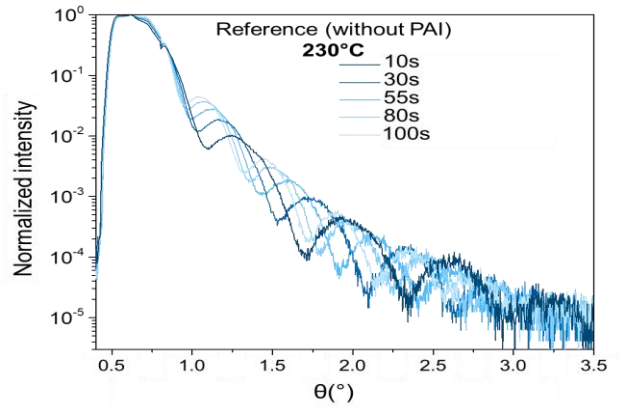

Fig. 1 : X-ray reflectivity curves (XRR) for the reference samples having undergone a thermal budget of 230°C for 10, 30, 55, 80 and 100 seconds.

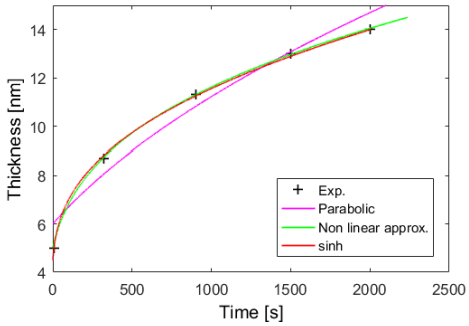

Fig. 2 : Fit of the experimental thickness for RTA annealing at 200°C of the reference sample using nonlinear reactive diffusion law (Eq. 1), parabolic law (Eq.2) and an approximation of the nonlinear law. The symbols represent experimental values.

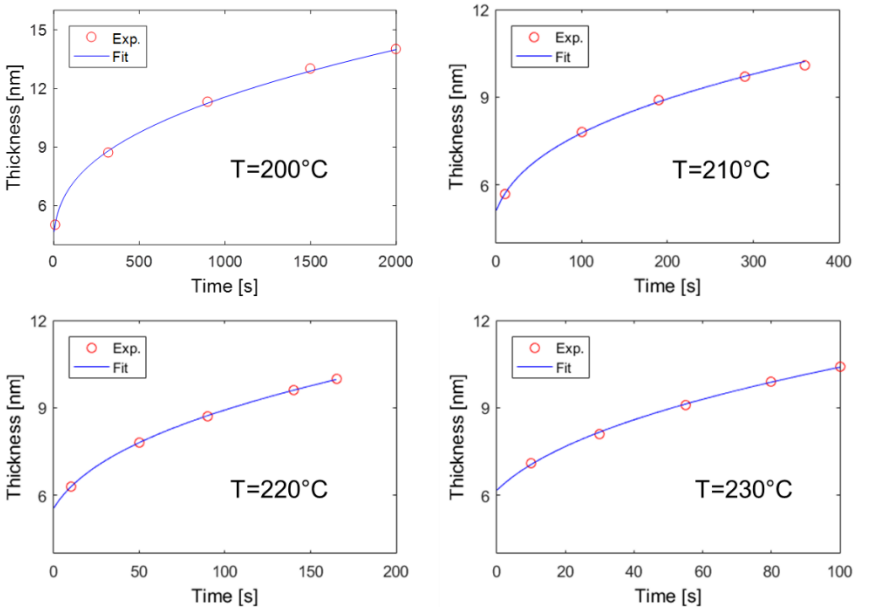

Fig. 3 : Simulation with the nonlinear reactive diffusion model (Eq. 1) of the evolution of the silicide thickness as a function of time for several temperatures of the RTA obtained experimentally for the reference sample without PAI.