Controlling Ni silicide formation by ion implantation

André Vantomme[a],*

[a] *Quantum Solid State Physics, KU Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*

Given its importance as contacting material, the formation of NiSi via the reaction of a Ni thin film with a Si substrate has been thoroughly investigated during the past decade. In order to keep up with the requirements imposed by the aggressively shrinking device dimensions, extensive efforts have been devoted to optimally tune the silicide properties in terms of resistivity, formation temperature, texture, thermal stability, etc. Approaches which have been taken include, amongst many others, alloying of the Ni with Pt or Pd. On the other hand, it has also become clear that the transient, metastable phases which appear during the early stages of the Ni-Si reaction, have a crucial impact on the reaction path, hence on the properties of the final phase of interest, i.e., NiSi.

To disentangle the role of these metastable silicides, we have focused on the use of ion implantation, a standard technique in device processing. The role of implantation is dual: on the one hand, it introduces impurities in the matrix (dopants), while on the other hand, damage (lattice defects) is created as a result of atomic collisions. Understanding the specific impact of impurity atoms and defects on the kinetics and/or thermodynamics of the silicide reaction path will allow one to tailor the metastable phases initially formed, and therefore the NiSi properties.

In order to differentiate between the various irradiation-induced effects, we have implanted either nitrogen (impurity) or argon (creating defects) to a range of fluences. The implantations were performed prior to thermal reaction, with an energy adjusted to either target the Si substrate, the Ni layer, or the interface region [1,2].

In this talk, we will focus on two metastable nickel silicide phases, i.e., the hexagonal Ni-rich phase (θ-phase) and the amorphous $Ni_{0.5}Si_{0.5}$ alloy, and review how these phases can be either stabilized or destabilized by ion implantation. To this end, we will detail on the specific role of the implantation-induced defects and the impurity atoms (i) on the phase formation sequence, (ii) on the reaction kinetics and (iii) on tuning the texture of the NiSi film (which has a major impact on the NiSi stability). We have found that these properties are to a large extent determined by a subtle interplay between the impurity concentration at the reaction front, their solubility in the various silicides, the occurrence of additional nucleation barriers, the grain orientation, a suitable template depending on the Si crystallinity… as well as the annealing conditions [1,2]. As an example, Fig. 1 shows how N implantation can result in the formation of an amorphous Ni-Si silicide, whereas Fig. 2 illustrates the impact of Ar implantation on the silicide formation temperature.

To disentangle the details of the silicidation, we have relied on a number of complementary characterization techniques, either *in situ* (synchrotron x-ray diffraction, Rutherford backscattering spectrometry, sheet resistance measurements…) or *ex situ* (Rutherford backscattering spectrometry, ion beam channelling, pole figure measurements, transmission electron microscopy…). In particular, the use of real-time techniques, i.e., investigating the phase formation and growth kinetics *during* the reaction, has shown to be particularly beneficial in order not to overlook any transient (but crucial) phases or amorphous phases (which escape detection with X-ray diffraction).

References
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2. K. van Stiphout, F. Geenen, N. Santos, S. Miranda, V. Joly, J. Demeulemeester, C. Mocuta, C.M. Comrie, C. Detavernier, L.M.C. Pereira, K. Temst and A. Vantomme, J. Phys. D: Appl. Phys. 54 (2021) 015307.

[*] *corresponding author e-mail: Andre.Vantomme@kuleuven.be*

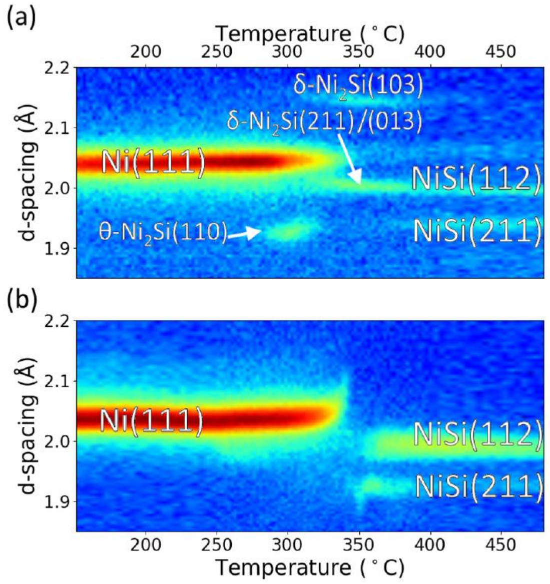

Figure 1: *In situ* XRD measurements of the reaction of a 35 nm Ni film on Si(100) for (a) an unimplanted sample and (b) a sample implanted with 1 × 10^{16} N cm^{-2} at 40 keV/atom. The absence of a diffraction peak in the temperature region between 330°C and 350°C for the implanted sample, originates from the formation of an amorphous Ni-Si layer.

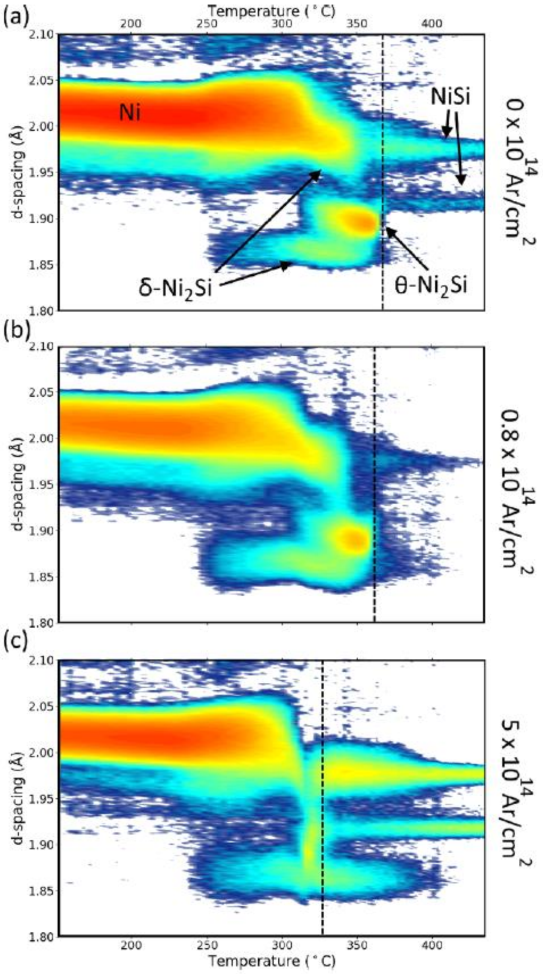

Figure 2: *In situ* XRD measurements of the reaction of a 13 nm Ni film on Si(100), for (a) an unimplanted sample, (b) a sample implanted with 0.8 × 10^{14} and (c) 5 × 10^{14} Ar cm^{-2} at 60 keV. The samples were annealed at a rate of 0.333°C/s. The silicide phases, as evidenced by their diffraction peaks, are indicated in (a). The dashed lines indicate the appearance of the NiSi phase, which occurs at lower temperature as the Ar concentration increases.