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Phase formation between Ni thin films and GaAs substrate

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ABSTRACT

In situ X-Ray Diffraction, X-Ray Reflectivity and High Resolution Transmission Electron Microscopy were used to investigate the sequence and the texture of phase formation during the solid-state reaction of Ni thin film with GaAs substrate. These results show the formation of a unique Ni_3GaAs crystalline phase at 200 °C that remains stable until 400 °C. The epitaxial relationships between this phase and the GaAs substrate were also evidenced. The formation of this unique phase, along with the variation of its lattice parameters when Ni is totally consumed, can be explained by local thermodynamic equilibrium and kinetics arguments.

Recent advances in III–V materials integration in functional devices (both MOSFET Metal-Oxide-Semiconductor Field Effect Transistor and photonic applications) [1–2] and the advances in the fabrication of high-quality GaAs/Si substrates [3], triggered the research on several device components. Moreover, such investigations can be extremely valuable for InGaAs-based MOSFET devices. Indeed, InGaAs substrates are similar to GaAs ones since Ga and In are completely miscible in the zinc-blende structure. Several studies have shown encouraging results on the feasibility of such high-performance devices [1,4]. Thus, studying the different fabrication processes on GaAs rather than InGaAs simplifies the understanding of the different phenomena that may occur. Among the different fabrication steps, the development of stable, reproducible, thin and low-resistive contacts is crucial to achieve functional devices. Historically, contacts on GaAs were made after a solid-state reaction between a metal and the GaAs substrate [5–6]. Among several elements or alloys, Ni proved to have interesting electrical properties as a reacting metal with the GaAs substrate [7–8]. However, although there was intensified research on the Ni-GaAs solid-state reaction at the end of the eighties until the mid-nineties [5,7,9–11], several discrepancies between the different authors resulted in significantly different sequences. Generally, the observed phases sequence included passing from an hexagonal Ni-rich phase to Ni_2GaAs, of the same structure, and finally the formation of hexagonal NiAs and cubic NiGa. Yet, different authors presented different phase sequences obtained by *ex situ* characterizations with various formation temperature and compositions. The nature itself of the B8-type structure of the Ni-GaAs intermetallic compounds makes it difficult to predict an exact phase composition as this phase includes generally a large domain of homogeneity [12]. Furthermore, the targeted dimensions for nowadays devices are much reduced compared to the ones studied before, and since texture, phase sequence and especially the intermetallic film stability can be impacted by the deposited metal thickness [13–14], the study of the formation of these intermetallic at reduced dimensions is needed.

Hence, we investigate in this work, the solid-state reaction between a thin film of Ni (20 nm) and a GaAs substrate for annealing temperatures going from 50 °C to 400 °C using state-of-the-art characterization techniques. *In situ* X-Ray Diffraction (XRD) and X-Ray Reflectivity (XRR) measurements have been carried out to characterize the sequence of phase formation. Finally, High Resolution Transmission Electron Microscopy (HRTEM) was carried out to measure the thickness of the intermetallic phase, its structure and the eventual epitaxial relationships of the formed layer with the substrate.

A thin layer of 20 nm of nickel was deposited on GaAs(100) wafer using a 99.9999% pure Ar gas flow to sputter a 99.99% pure Ni target, in a commercial magnetron sputtering system exhibiting a base pressure of 10^{-8} Torr. The GaAs(100) substrate was cleaned with diluted nitric acid HNO_3 prior the Ni deposition.

In situ measurements were carried out on a two-circle X'Pert diffractometer. As-deposited sample was mounted on an adapted furnace and was annealed under secondary vacuum from 50 °C to 400 °C using a step of 10 °C. At each step, XRD measurements were carried out with a wavelength of 1.54 Å. *Ex situ* XRR was used to measure the thickness, density and roughness of the thin layers deposited on a substrate in a range of a few nanometres.

In order to investigate the early stages of phase formation by Transmission Electron Microscopy (TEM), two samples were prepared in the following manner: using the same furnace and annealing conditions as

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for the *in situ*-annealed sample, two samples were annealed from 50 °C up to respectively, 150 °C and 180 °C. Finally, the analysis has been completed by High Resolution TEM imaging. The cross-section TEM images of samples show the interface between the Ni layer and the GaAs substrate. The so-formed phase is identified from the Fast Fourier Transforms (FFT) of the HR-TEM images [15].

The purpose of the *in situ* XRD experiment described above is to follow the evolution of the formed phase after a solid-state reaction between the Ni metallic film and the GaAs substrate. The different XRD patterns were acquired during annealing between 50 °C and 400 °C using steps of 10 °C. The result is given in the form of an intensity colour map in Fig. 1a. The X axis carries the 2θ angle, the Y axis carries the annealing temperature and the intensity is represented by a colour level code.

On Fig. 1a, up to 190 °C, the only measured peaks correspond to the deposited Ni film and the TiN protective layer. Starting from 190 °C, the Ni peak disappears rapidly and two peaks appear at $2\theta = 31.59°$ and 65.85°. These planes correspond respectively to the $\{10\bar{1}1\}$ and $\{20\bar{2}2\}$ planes of a hexagonal structure as reported by literature [16]. A shift towards higher 2θ values is observed for these planes. From these *in situ* XRD measurements, the evolution of the interplanar distances of the $10\bar{1}1$ peaks with the annealing temperature was deduced and presented in Fig. 1b. From this figure, the interplanar distance is seen to decrease with temperature.

While some authors measured the first phase to form as "Ni_2GaAs", others measured the first phase as being "Ni_3GaAs". To eliminate the ambiguity about the nature of the formed intermetallic phase, the expected volumetric ratios $V_{NixGaAs}/V_{Ni}$ (x is the number of Ni atoms in the intermetallic phase) have been calculated for both Ni_2GaAs and Ni_3GaAs phases, where $V_{NixGaAs}$ is the unitary volume of Ni_xGaAs and V_{Ni} is the atomic volume of Ni [17]. Indeed, in order to form a layer of the Ni_2GaAs phase, the thickness of the so-formed phase should increase by a factor of three with respect to the thickness of the consumed Ni ($V_{NixGaAs}/V_{Ni} = 3$). However, in the case of Ni_3GaAs, the thickness of the so-formed phase should increase by a factor of two relative to the thickness of the consumed Ni ($V_{NixGaAs}/V_{Ni} = 2$). XRR analysis on two samples (shown on Fig. 2a), one after deposition and the second after annealing at 400 °C allowed to measure the thickness of the different layers.

From the fitting of the XRR patterns of the as-deposited sample and the annealed sample at 400 °C, we deduce that the thickness of the TiN protective layer, of the deposited Ni layer and that of the so-formed phase at 400 °C are respectively (17 ± 1) nm, (21 ± 1) nm and (43 ± 1) nm. Hence 43 nm of Ni_xGaAs is formed from 21 nm of Ni, which corresponds to a volumetric ratio of $V_{NixGaAs}/V_{Ni} = 2$. Thus,

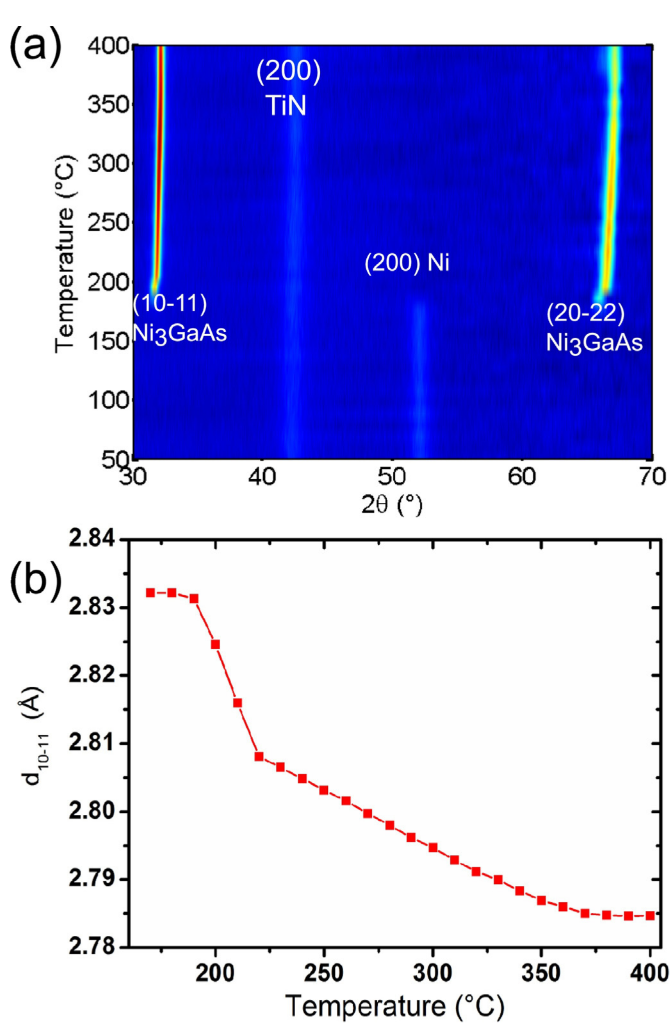

Fig. 1. (a) *In-situ* XRD diagrams (λ = 1.54 Å) performed on 21 nm of Ni on GaAs (100) during annealing between 50 °C and 400 °C by steps of 10 °C with a 5 °C min^{-1} ramp and an overall time of 5 min for XRD measurements, (b) Evolution of the interplanar distances of the (10–11) peaks with the annealing temperature deduced from *in-situ* XRD diagrams.

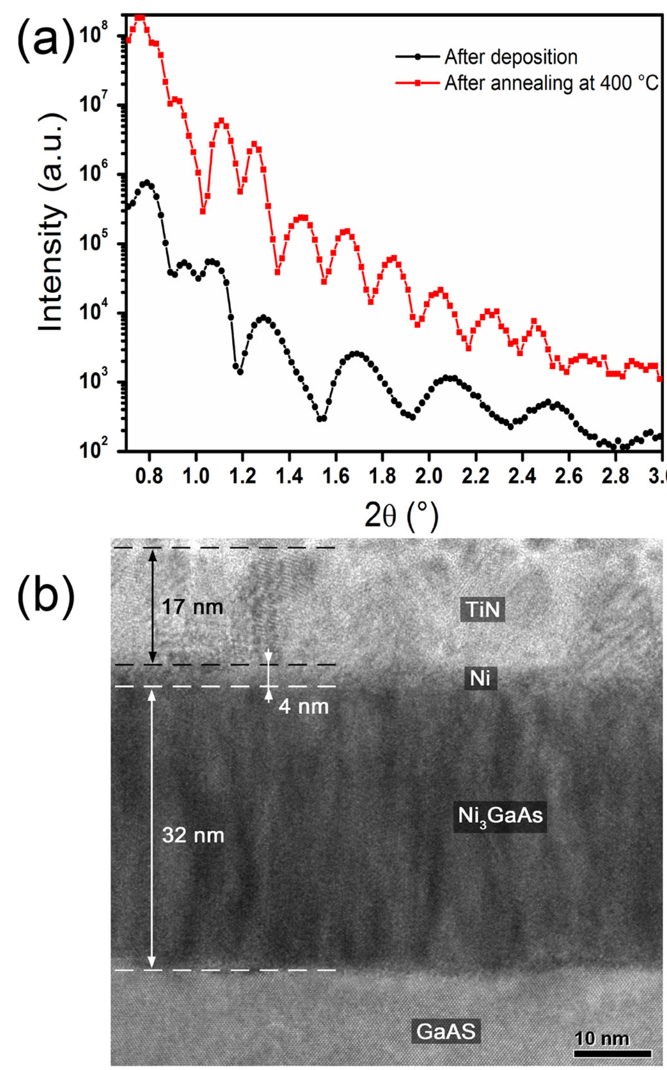

Fig. 2. (a) XRR spectrums of the sample just after Ni deposition and after annealing at 400 °C, (b) TEM Cross section image obtained after sample annealing at 150 °C in the *in-situ* XRD chamber using the same conditions as described in Fig. 1a.