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Phase formation in intermixed Ni–Ge thin films: Influence of Ge content and low-temperature nucleation of hexagonal nickel germanides

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ABSTRACT

In this study, we focus on phase formation in intermixed Ni–Ge thin films as they represent a simplified model of the small intermixed interface layer that is believed to form upon deposition of Ni on Ge and where initial phase formation happens. A combinatorial sputter deposition technique was used to co-deposit a range of intermixed Ni–Ge thin films with Ge concentrations varying between 0 and 50 at.%Ge in a single deposition on both Ge (100) and inert SiO_2 substrates. *In situ* X-ray diffraction and transmission electron microscopy where used to study phase formation. In almost the entire composition range under investigation, crystalline phases where found to be present in the as-deposited films. Between 36 and 48 at.%Ge, high-temperature hexagonal nickel germanides were found to occur metastabily below 300 °C, both on SiO_2 and Ge (100) substrates. For Ge concentrations in the range between 36 and 42 at.%, this hexagonal germanide phase was even found to be present at room temperature in the as-deposited films. The results obtained in this work could provide more insight in the phase sequence of a pure Ni film on Ge.

1. Introduction

The continuous scaling down of microelectronic devices pushes the current Si-based technology to its limits. Alternative materials are being investigated to replace Si in e.g. the gate regions of Metal-Oxide-Semiconducter Field Effect Transistors (MOSFET). According to the industry roadmap, Ge is a top candidate to replace Si in p-channel MOSFET devices due to its higher carrier mobility and relative compatibility with silicon processing [1]. Similar to the current SALICIDE (Self-Aligned Silicide) process, where metal silicides are used to contact the source, gate and drain regions of MOSFETs, metal germanides appear as natural candidates for contacting Ge. A systematic study of germanide formation and properties in 20 transition metal on Ge systems by Gaudet et al. [2], revealed NiGe as the most promising contact material since it exhibits the most suitable properties among all investigated metal germanides, including low formation temperature, low resistivity and a wide stable temperature window during ramp anneals.

If we are to use NiGe as a contact material in future devices, a thorough understanding of the formation mechanisms and properties of the different germanides in the Ni–Ge system is important. For the bulk system, most of the work on this binary Ni–Ge system was done in the 1970s [3,4] and was summarized in 1987 by Nash and Nash [5], which led to the Ni–Ge binary phase diagram as it is known today (see Fig. 1). For the thin film system, detailed studies on the phase formation upon annealing of a thin Ni film on Ge using *in situ* X-ray diffraction (XRD) were performed by Gaudet et al. [6] and Nemouchi et al. [7]. Both groups reported the simultaneous growth of NiGe and Ni_5Ge_3 on Ge (100), where Ni_5Ge_3 only exists over a small temperature window since it is consumed by the growth of NiGe, which is the stable end phase. However, the existence of other Ni-germanides in this intermediate region could not be ruled out due to overlapping peak positions of different Ni-rich germanides [6]. Interestingly, Jensen et al. [8] reported on the metastable nucleation of the high temperature ϵ-Ni_5Ge_3 when annealing ratio-controlled Ni–Ge multilayers on an inert SiO_2 substrate.

In order to fully understand the phase formation in the Ni–Ge system, more information on this Ni-rich phase region is required. In the Ni–Si system, a similar region of transient Ni-rich phases during a ramp anneal of a thin Ni film on Si can be observed. Recently, a detailed study of a ratio-controlled Ni–Si system was performed in our group to gain more insight in the early phase formation in the Ni–Si system, which led to the identification of the metastable hexagonal θ-phase in the Ni on Si phase sequence

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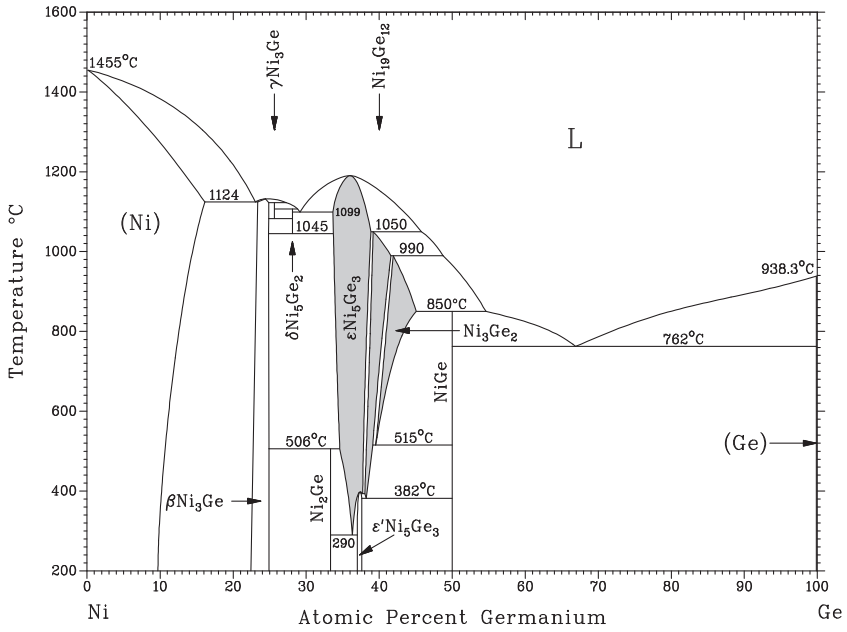

Fig. 1. Equilibrium phase diagram of the Ni–Ge system. This study focuses on the 0–50 at.%Ge composition region. (taken from [5]).

[9–12]. In this paper, we present a similar study of phase formation in the Ni–Ge system. Ratio-controlled Ni–Ge films were deposited on both SiO_2 and Ge (100) substrates and *in situ* XRD was used to monitor phase formation during linear ramp anneals.

2. Experimental

Intermixed Ni–Ge films with varying Ge concentrations (from 0 to 50 at.%Ge) were deposited on both 100 nm thermal SiO_2 and HF-cleaned p-type Ge (100) substrates using a combinatorial sputter deposition technique. Substrate strips with a length of 15 cm and a width of 1–2 cm were mounted on a rotating carousel in a deposition chamber with a base pressure of 2×10^{-7} mbar. During co-sputtering of Ni and Ge, spatial control of the separate material fluxes resulted in a Ge film with a thickness gradient being intermixed with a uniform Ni film. The deposition parameters were tuned in such a way that the Ni content in the resulting film is constant and corresponds to the amount of Ni in a pure 50 nm Ni film (i.e. about 45×10^{16} atoms/cm^2). The outcome of such a single deposition is a 15 cm long strip with a Ni-Ge film in which the Ge concentration varies from 0 to 50 at.%. This gradient is then cleaved into individual 5 mm long samples for further characterization. This effectively results in 29 samples per deposited strip with a composition difference of ~ 2 at.% between consecutive samples and a Ge concentration uniformity of ± 1 at.% within a single sample. The composition of all samples was verified with Rutherford Backscattering Spectrometry (RBS).

Germanide phase formation was studied using a home-built *in situ* XRD setup, consisting of an experimental heating chamber mounted in a Bruker D8 Discover XRD system. All individual samples were subjected to a ramp anneal at 3 °C/s from room temperature up to a temperature of 800 °C or 650 °C for the samples on SiO_2 and Ge (100) respectively. During the anneal, the diffraction pattern was recorded every 3 s over a range of 20 ° in 2θ.

High Resolution Transmission Electron Microscopy (HR-TEM) was performed on a FEI Tecnai G2 electron microscope, operating at 200 kV. Sample preparation was done using mechanical polishing followed by ion milling.

3. Results

3.1. Ni (Ge) on inert SiO_2 substrates

Due to the inert SiO_2 substrate, the Ni–Ge layers have a fixed Ni/Ge composition throughout the anneal. As can be expected from the phase diagram (Fig. 1), the amount of Ge in the Ni (Ge) mixture will have an influence on the initial crystallization temperature and the first forming phase. Here, *in situ* XRD was used to probe the phase formation sequence while heating the samples to 800 °C.

Fig. 2(a) shows selected *in situ* XRD measurements with 2θ on the vertical axis and temperature on the horizontal axis. The measured XRD intensity is plotted as a logarithmic grayscale map (with black corresponding to the highest intensity). To illustrate the procedure of identifying the phase formation sequence, we will discuss the second *in situ* XRD scan, i.e. the scan of the sample with 33 at.%Ge. From room temperature on, three peaks are clearly visible, indicating the presence of a crystalline phase in the as-deposited film. All these peaks can be attributed to Ni_2Ge: the peak at $2\theta = 41.3°$ can be indexed as Ni_2Ge (103), the intense peak around $2\theta = 44°$ is a superposition of Ni_2Ge (031) and Ni_2Ge (211) and the third peak around $2\theta = 47.5°$ can be indexed as a superposition of Ni_2Ge (020) and Ni_2Ge (113). Around 550 °C, a phase transformation occurs as indicated by the disappearance of the three Ni_2Ge peaks and the emergence of three new peaks. The new features at $2\theta = 43.8°$ and 51°can be identified as β-Ni_3Ge (111) and β-Ni_3Ge (200) respectively. The third peak around $2\theta = 45°$ however is not that straightforward to identify, since it can be indexed as either ϵ-Ni_5Ge_3(102), Ni_3Ge_2(102) or $Ni_{19}Ge_{12}$(212). A complementary *in situ* XRD scan (not shown here) in a different 2θ window revealed a second peak around $2\theta = 30.5°$ which can similarly be attributed to the (101) peak of either ϵ-Ni_5Ge_3 or Ni_3Ge_2 or to $Ni_{19}Ge_{12}$(200). Similar identification difficulties of these specific phases, which exist over a broad composition range in the binary Ni–Ge phase diagram (refer to the shaded area in Fig. 1), were encountered in a vast subset of the measured samples. This identification problem can be related to the very closely related crystal structures of these three phases [3,13], which makes it nearly impossible to discern between them based solely on powder XRD