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Ni silicide study at the atomic scale: Diffusing species, relaxation and grooving mechanisms

M. El Kousseifi,* K. Hoummada and D. Mangelinck

Aix-Marseille University, CNRS, IM2NP, Case 142, 13397 Marseille Cedex 20, France

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Abstract—A thin layer of Ge (1 nm) deposited between a 30 nm Ni film and a (100)Si substrate was used as a marker for the diffusing species during Ni silicide formation. In situ X-ray diffraction heat treatments with temperatures ranging from 150 to 400 °C were performed to show the specific steps of silicide formation. Atom probe tomography (APT) enabled the diffusing species during the Ni deposition and during the formation of δ-Ni_2Si and NiSi phases to be determined. APT measurements of the redistribution of Ge during the stress relaxation of δ-Ni_2Si and during the formation of NiSi highlighted the mechanisms of stress relaxation and morphological degradation of NiSi.
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1. Introduction

Ni-based self-aligned silicide is widely used as contacts and interconnections in ultra-large-scale integrated circuits [1]. It is obtained by a solid-state reaction between an Ni thin film and an Si substrate. This reaction leads to the formation of δ-Ni_2Si as the first phase, followed by NiSi at relatively high temperatures, and the $NiSi_2$ phase at higher temperatures. Therefore, the fundamental mechanisms related to their formation, including the phase formation sequence, the growth kinetics and the microstructures of the silicide, are of great interest for applications. NiSi is the desired phase in Ni silicides as a contact material in advanced integrated circuits [2], because of several advantages: low resistivity, low temperature formation, low consumption of Si and compatibility with SiGe. However, a major disadvantage of NiSi is its degradation at high temperature. Two degradation mechanisms can be distinguished: the formation of the resistive phase $NiSi_2$ and, more crucial for applications, the agglomeration of thin NiSi films [3]. One possibility to delay the NiSi phase agglomeration is through the addition of a percentage of Pt to Ni, which significantly increases the morphology stability of NiSi on Si substrates and retards the formation of the $NiSi_2$ phase [4–6]. The incorporation of SiGe alloy was found to improve the performance of MOSFET transistors by increasing the carrier mobility of Ge (channel) and by reducing the contact resistance of the source and drain. Low-resistivity electrical contacts can also be made to the Ge-containing regions by the same process as that for Si (i.e. using the Ni-based self-aligned silicide). However, experimental results show generally worsened morphological stability for the ternary silicide $NiSi_{1-x}Ge_x$ [7], and this could be related to the presence of Ge in the NiSi phase and a higher mobility of Si and Ge inside this phase at 400–500 °C [8,9] compared with the mobility of Si in NiSi. Moreover, roughening in the polycrystalline NiSi(Ge) phase can be caused by thermal grooving at grain boundaries via diffusion away from the high-energy interfaces [10], and this grooving mechanism is not well understood in the Ni–Si–Ge system.

In addition, during the formation of silicides, an intrinsic stress is developed as a result of the difference in volume between one reactant (either Si or M “Metal”) and the product (silicide). This stress development is usually accompanied by a relaxation of the stress. A theoretical model was developed to describe the evolution of the strain, taking into account these two phenomena [11]. Two relaxation mechanisms have been proposed [12]: the first suggests the diffusive motion of the atoms of the species in the phase, and the second is based on the generation and the motion of dislocations in the silicide. Recently, it has been shown that the formation of NiSi depends on the strain in δ-Ni_2Si, i.e. δ-Ni_2Si has to be relaxed before NiSi starts to form [13]. However, stress relaxation needs more dedicated experiments to improve understanding of its mechanism.

From both fundamental and application points of view, it is important to identify the main diffusing species during the formation of silicide. Markers such as Si radiotracers or implanted gas atoms can be used to identify the diffusing

* Corresponding author. Tel.: +33 491282710; e-mail: mike.elkousseifi@im2np.fr

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species during silicide formation [14]. Each of these markers has some issues: in the case of Si radiotracers, their very short lifetime limits their use. For the implanted gas, the accuracy is not so good, since it is quantitative for diffusivity ratios between 0.1 and 10. Otherwise, only qualitative results could be obtained outside this range [14]. Another type of tracers concerns pairs of atoms that have very similar properties and thus can act like true isotopes. Such well-known pairs are constituted by silver and gold or silicon and germanium, for example. One of the techniques used to study the markers is Rutherford back scattering (RBS), but not all markers can be studied by this technique (a good marker for RBS should have a higher mass than the silicide metal). Some markers require Auger electron spectroscopy or secondary ion mass spectroscopy.

For Ni silicide formation, markers such as Si radiotracers [15,16] or implanted gas atoms [17,18] were used to identify the diffusing species. Ge was also found to be a good isotope-like marker for monitoring the diffusion of Si in NiSi [19]. Otherwise, it is worth noting that Ni is the dominant diffusing species during the diffusion-controlled growth of δ-Ni_2Si and NiSi [20,21]. Marker experiments [17,22,23] have shown that, during the formation of δ-Ni_2Si and NiSi, the diffusion coefficients of Ni atoms in these two silicides are at least ten times greater than those for the Si atoms. These two Ni silicide phases can be considered to form through metal motion.

For the ultra-thin films, atom probe tomography (APT) is a powerful technique to study markers in the silicide at an atomic scale. Indeed, APT is an analytical characterisation technique that enables the position and the identity of all elements in a small needle-shaped specimen to be determined with sub-nanometre resolution [24,25]. APT delivers very high spatial resolution (sub-0.3-nm) three-dimensional (3-D) compositional information [26], and it is a tool well suited to characterising interfacial composition [27,28], segregation on dislocation [29,30] and precipitation phenomena [31].

In the present study, 1 nm of Ge was deposited between the 30-nm Ni film and the Si substrate in order to use it as a marker for the diffusing species during Ni silicide formation. In situ X-ray diffraction (XRD) heat treatments with temperatures ranging from 150 to 400 °C were performed to find the phase sequence. The APT analysis reveals the diffusing species during Ni deposition and the following heat treatment when δ-Ni_2Si and NiSi formed. APT analyses after δ-Ni_2Si relaxation give an indication of its relaxation mechanism. The redistribution of Ge atoms during the formation of the NiSi phase at higher temperatures was also investigated.

2. Experimental

Since Si oxidises quickly and the native oxide prevents diffusion and reaction between Si and Ni from happening, the Si substrate was immersed in 5% diluted HF for 1 min to remove the native oxide. Then, the substrate was directly placed in the PVD deposition chamber, where the deposition by magnetron sputtering with a base pressure of ∼10–8 torr using 99.999% pure Ar gas flow was performed. As a marker for the diffusing species during growth, 1 nm of Ge was first deposited at room temperature on the Si substrate and covered by 30 nm of Ni. For comparison, a 30-nm-thick Ni film without Ge was also deposited on a Si substrate. After deposition, the samples were cut into several pieces of size 2 × 1.5 cm. The first piece was analysed directly after deposition to study the initial state of the system, and the others were loaded into the in situ XRD chamber equipped with a heating stage under a vacuum of $\sim 10^{-5}$ mbar. The annealing for in situ XRD analysis was performed by first ramping from room temperature to 150 °C at a rate of 35 K min^{-1}; then from 150 °C to the chosen temperature, a XRD scan was made after each 5 °C temperature increment. The ranging rate between two steps was 5 K min^{-1}. A wide annealing ranging from 150 to 400 °C was first used, and several temperatures (220, 250, 325, 400 °C) shown in Fig. 1b were reselected to study specific steps of the silicide formation. APT analysis was made on each sample after annealing: for this, the APT specimen preparation was performed using a Helios dual-beam focused ion beam equipped with a micromanipulator and with a gas injection system for Pt deposition. Several steps for the APT specimen preparation by FIB were needed, as described elsewhere [26,31]. Prior to FIB preparation, the samples were covered with a 100 nm Ni protection layer deposited by physical vapour deposition (PVD) and then by ∼100 nm of Pt by ion-assisted deposition to prevent Ga contamination during the process. Once the region of interest was adequately protected, a classical trench milling around the Pt defined zone was performed; the wedge was then extracted from the substrate using the micromanipulator and placed on an APT support post. The last step was to obtain an appropriate needle-shaped specimen from the wedge slice mounted on the support post by a sequence of annular milling applied to the specimen. As a final step, a low-energy (2–5 keV) ion beam was used to clean the top of the sample.

The APT analyses were carried out in a LEAP 3000X HR instrument. The laser pulsing rate was set at 100 kHz, and the detection rate was kept at 0.002 event/pulse by increasing the applied voltage. The specimen temperature and the laser energies were set between 20 and 50 K and between 0.3 and 0.6 nJ, respectively. Data reconstruction was done with commercial IVAS software.

3. Results

In situ XRD measurements were first performed for the whole temperature range (150–400 °C) to show the formation sequence of Ni silicide phases for the two types of samples (Ni/Si and Ni/Ge/Si). Fig. 1a and b shows similar features, indicating a similar sequence of phases for both samples. The formation sequence starts with the growth of the δ-Ni_2Si phase at the expense of the Ni film. During the growth of δ-Ni_2Si, the transient phase θ-Ni_2Si appears at ∼220 °C and then disappears at ∼270 °C. Finally, NiSi appears at 270 °C and then grows at the expense of the δ-Ni_2Si phase. Only the NiSi phase exists at the end of annealing. Furthermore, all Ni silicides present the same XRD peaks, even if a small change in intensity may be formed. The Ni silicides formed in both samples thus have, in addition to similar phase sequence formation, very similar orientations (Fig. 1). These XRD experiments indicate that the Ge marker at the Ni/Si interface induces only slight changes in kinetics, but does not significantly affect the formation sequence of Ni silicide. Thus, the Ge layer can

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