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Atomic-scale redistribution of Pt during reactive diffusion in Ni (5% Pt)–Si contacts

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ABSTRACT

The NiSi silicide that forms by reactive diffusion between Ni and Si active regions of nanotransistors is used nowadays as contacts in nanoelectronics because of its low resistivity. Pt is added to the Ni film in order to stabilise the NiSi phase against the formation of the high-resistivity $NiSi_2$ phase and agglomeration.

In situ X-ray diffraction (XRD) experiments performed on material aged at 350 °C (under vacuum) showed the complete consumption of the Ni (5 at% Pt) phase, the regression of Ni_2Si phase as well as the growth of the NiSi phase after 48 min. Pt distribution for this heat treatment has been analysed by laser-assisted tomographic atom probe (LATAP). An enrichment of platinum in the middle of the NiSi phase suggests that Pt is almost immobile during the growth of NiSi at the two interfaces: Ni_2Si/NiSi and NiSi/Si. In the peak, platinum was found to substitute for Ni in the NiSi phase. Very small amounts of Pt were also found in the Ni_2Si phase close to the surface and at the NiSi/Si interface.

1. Introduction

The formation of nanometric phases by reactive diffusion between a thin film and a substrate is a fundamental problem that has considerable interest for applications. This is particularly true for silicides due to their use as contacts in microelectronic devices. These silicides are formed through the self-aligned salicidation process.

Thin film reactions [1] are mainly characterized by sequential growth, the lack of certain equilibrium phases, and sometimes the growth of metastable phases while the simultaneous parabolic growth of all the equilibrium phases is usually observed in bulk interdiffusion couples. Nucleation [2] has been shown to play a crucial role in the formation of some phases and, in particular, the silicon-rich silicides ($NiSi_2$, $TiSi_2$). The addition of alloying elements may influence the formation and nucleation of silicides. For example, the addition of 5% Pt to a Ni film was shown to stabilise the low-resistivity NiSi phase through an increase of approximately 150 °C of the temperature of formation of $NiSi_2$ [3]. As $NiSi_2$ has a higher resistivity, this Pt addition allows for a better integration of NiSi as contacts for nanometric transistors [4]. Over the last few years, there has been an extensive work on determining the effects of alloying element on the formation and stability of Ni silicides [5]. However, the redistribution of alloy elements during the formation of silicide is not well understood. One of the reasons is the difficulty of mapping out the distribution of alloying elements at the nanometric scale. Advanced characterization methods with very high spatial resolution are thus required to analyse the redistribution at the nanoscale. Laser-assisted atom probe tomography (APT) has been developed in this goal [6–9]. Thompson et al. [10] reported the observation of the NiSi and Ni_2Si phases after heat treatment at 350 °C for 10 min. Phase formation and platinum redistribution were previously studied in Ni (5% Pt) films after deposition [11] and after heat treatment at 290 °C [12]. The first study corresponds to silicide formation during deposition and the second to the simultaneous formation of Ni_2Si and NiSi. To complete the study of platinum redistribution, it is important to look at another step in silicide formation, namely the growth of NiSi at the expense of Ni_2Si.

In this paper, we thus studied the redistribution of Pt after a heat treatment at 350 °C for 48 min using the laser-assisted tomographic atom probe (LATAP), X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

2. Experimental

Films of polycrystalline Ni, 80 nm thick, containing 5 at% Pt were deposited at room temperature (RT) by co-sputtering of Ni

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and Pt targets on {1 0 0} *p*-doped Si substrates (resistivity 0.01 Ω cm). The $Ni_{1-x}Pt_x$ films were deposited simultaneously on (i) blanket substrate for characterization by XRD and conventional TEM and (ii) high aspect ratio flat-topped {1 0 0} silicon posts for APT analysis. XRD were performed using the Bragg–Brentano geometry [13] and a CuKα source. An isothermal heat treatment was performed in a vacuum chamber attached to the XRD diffractometer. The temperature of 350 °C was reached with a ramp of 30 K/min and the vacuum in the chamber was in the range of 10^{-4} Pa. During annealing at 350 °C, XRD scans of duration 16 min were continuously recorded with a scan rate of 0.6°/min. This made it possible to follow the temporal evolution of peaks diffraction and thus to study in situ silicide formation. Heat treatment was stopped when the Ni_2Si peak intensity started to decrease. In the APT technique, a tip is evaporated atomic layer by atomic layer and analysed by time-of-flight mass spectrometry, allowing a small volume of material (typically $15 \times 15 \times 200\,nm^3$) to be reconstructed in the three dimensions of space, atom by atom, on a nearly atomic scale. A protective layer of Cr (200 nm) was first deposited on the surface of posts to prevent damage due to Ga irradiation. Then the region of interest of silicon posts was transformed into a tip with 30 keV Ga^+ focused ion beam milling. Tips were finally cleaned with a 2 keV gallium beam. The APT experiments were carried out using femtosecond laser pulses (wavelength 515 nm, duration 350 fs) and with the energy of about 0.3 μJ.

3. Results and discussion

Fig. 1 shows the XRD results after deposition and after isothermal annealing at 350 °C for various times. The XRD spectrum for the as-deposited samples shows a peak for $Ni_{1-x}Pt_x$ and a small bump at 47.3° that may correspond to the (2 1 1) NiSi reflexion. This suggests that the NiSi phase is formed during deposition of the nickel alloy on silicon wafers in accordance with our previous results by APT [11]. The phase that forms during deposition at ambient temperature has been reported to be amorphous [16,17]. The low XRD intensity can be in agreement with an amorphous phase but it is very difficult to draw conclusion from such a bump. The formation of this phase can be explained by the large driving force for nucleation during deposition added to the presence of the condensation heat of Ni on Si substrate (approximately 420 kJ/mol [14,15]).

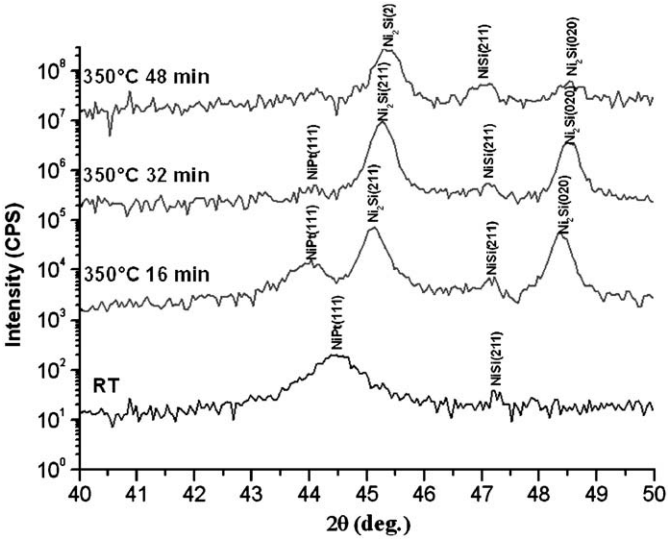

Fig. 1. XRD spectra (CuKα source; Bragg–Brentano geometry) of $Ni_{0.95}Pt_{0.05}$/Si(1 0 0) as deposited and annealed at 350 °C for different times: 16, 32, and 48 min.

After 16 and 32 min of annealing, the XRD spectra show peaks for Ni_2Si, NiSi, and $Ni_{1-x}Pt_x$. The simultaneous presence of Ni_2Si and NiSi together with the $Ni_{1-x}Pt_x$ solid solution implies a simultaneous growth of these two phases. This confirms the results obtained by APT for a 290 °C heat treatment [12].

Finally, after 48 min of annealing, the intensities of Ni_2Si (2 1 1) and Ni_2Si (0 2 0) decrease. Ni_2Si silicide is consumed to form NiSi silicide and the complete consumption of $Ni_{1-x}Pt_x$ is observed. In order to study the redistribution of Pt during the growth of NiSi at the expense of Ni_2Si, the heat treatment was stopped at this stage.

The TEM image (Fig. 2) obtained for the blanket substrate show that the silicide layers are not uniform and that they exhibit rather large roughnesses. In particular, the Ni_2Si layer varies from a few tens of nm to a few nm in thickness. It is therefore difficult to determine precisely the thickness of Ni_2Si and NiSi phases. The diffraction pattern shows spots belonging to Ni_2Si and NiSi. At this stage, NiSi is thus not anymore amorphous but polycrystalline.

Several tips were extracted from different posts in this sample and analysed by APT. Figs. 3 and 4 show typical LATAP reconstructions obtained for this sample. The distribution of Ni and Si atoms (Fig. 3) exhibits the presence of two intermixed regions: the first region is richer in Ni than the second region. Depth profiles derived from these images (Fig. 3b) reveal that Ni_2Si and NiSi phases formed as a consequence of the reactive diffusion between Ni (5 at% Pt) and the Si substrate at 350 °C. The average concentration of Ni, Si, and Pt elements in the Ni_2Si and NiSi phases is given in Table 1.

The first and second interface, Ni_2Si/NiSi and NiSi/Si (not shown here), appear curved, suggesting a rather large roughness of interfaces in agreement with the TEM images (Fig. 2).

Fig. 3a indicates that Pt is accumulated near the surface of the Ni_2Si phase. The concentration of Pt in Ni_2Si is around 1 at% close

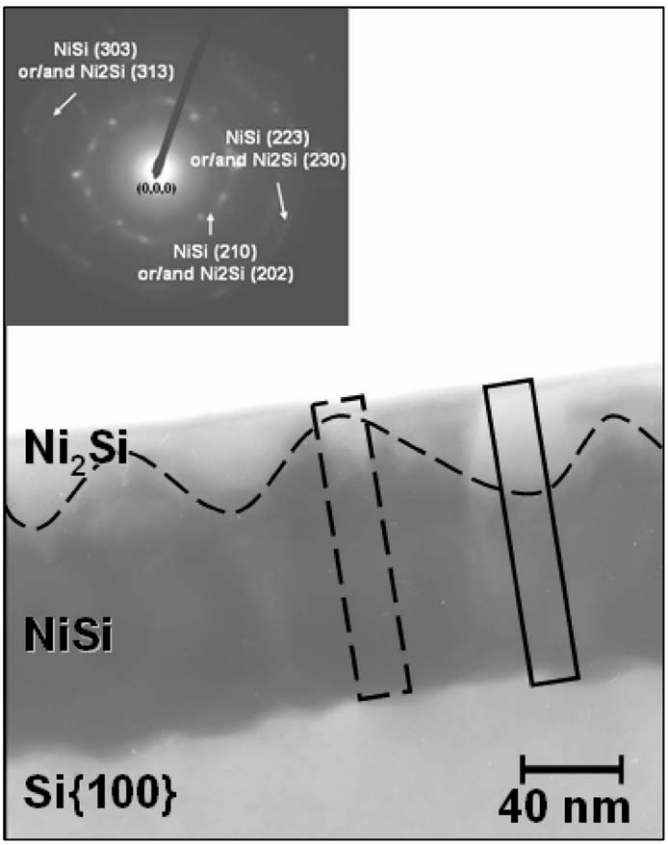

Fig. 2. Conventional TEM image of $Ni_{0.95}Pt_{0.05}$/Si (1 0 0) silicided at 350 °C for 48 min and corresponding diffraction pattern.