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Growth and characterization of Pt-Si droplets for silicon nanowires synthesis

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ABSTRACT

The formation of platinum silicide phases as a function of the annealing temperature was investigated using *in-situ* real-time Rutherford backscattering spectrometry. The *in-situ* real-time RBS revealed the reaction of platinum and silicon to start at about 220 °C to form platinum silicide phases, Pt_2Si and PtSi in sequence. Scanning electron microscope revealed the morphological change in the platinum layer (formation of droplets) at 800 °C. The particle induced X-ray emission analysis showed the variation of platinum intensity, in the droplets areas, between 1600 and 2000 counts. The surrounding areas are left almost uncovered due to platinum film dewetting. In-plane as well as out-of-plane silicon nanowires were observed to form at 800 °C and 1000 °C using pulsed laser ablation and thermal annealing techniques, respectively.

1. Introduction

Synthesis and application of silicon nanowires (SiNWs) have gained much interest over decades in the area of thin film-based devices due to their low dimensional properties [1,2]. Depending on the synthesis technique and intended application, SiNWs can grow lateral [3–5] and perpendicular [6] to the silicon substrate, with both vapour-liquid-solid (VLS), vapour-solid-solid (VSS) and solid-liquid-solid (SLS) growth mechanisms applicable. Therefore the process of producing these nanostructures requires better understanding of the metal-silicide seed nucleation on silicon (Si) template substrates. Solid-state dewetting has been reported to be an innovative method of producing well-ordered nucleation metal silicide seeds necessary to catalyse nanowire growth [7]. The seeds are prepared by depositing a metal catalyst (thin film of few nanometres) onto the Si substrate followed by annealing at high temperatures [8]. In this study, a n-type Si ⟨1 0 0⟩ wafer was used as a substrate and a platinum (Pt) coating as a catalyst. The formation of the silicide as a function of temperature was analysed using *in-situ* real-time Rutherford backscattering spectrometry (RBS). The elemental distribution of Pt in the droplet regions was analysed using particle induced X-ray emission (PIXE) while the micrographs of the annealed samples as well as silicon nanowires were acquired using a scanning electron microscope (SEM).

2. Preparation of Pt coating and analysis methods

A 20 nm thick Pt film was deposited on four silicon substrates (1 cm × 1 cm) using an electron beam evaporator, at a vacuum pressure of 5×10^{-6} mbar and a deposition rate of 0.8 Å/s. The substrates were ultrasonically cleaned in a sequence of several solvents (methanol, acetone, trichloroethylene, acetone, methanol and de-ionized water) for the duration of 10 min for each step.

An *in-situ* real-time Rutherford backscattering spectrometry (RBS) experiment was conducted on the first sample using 2 MeV alpha particles at a backscattering angle of 165°, a beam spot size of 2 mm and in a vacuum of 5×10^{-6} mbar. The data was collected using a surface barrier detector (with 20 keV resolution) and the angle between the sample surface and the incident beam was-10°. The sample was mounted on a flat copper surface heating stage with a thermocouple mounted at the back. The thermal annealing was carried out with linear temperature ramping from room temperature (RT) to 360 °C at 2 °C per minute. *In-situ* real-time RBS spectra were extracted at different temperatures (230 °C, 300 °C and 350 °C) and simulated using Rump software [9].

For the formation of droplets, the second sample was annealed at 800 °C for 30 min, below the eutectic point of PtSi + Si (978 °C) using a STF 1200 series split tube furnace. Two other samples were

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used for nanowires growth; one was annealed at 1000 °C for 10 min while flowing argon gas at a flow rate of 250 millilitres per minute (ml/m), the other sample, silicon was deposited using pulsed laser deposition (PLD) techniques with a 255 nm wavelength laser (Nd:YAG) at 800 °C. The surface morphologies of all the samples were investigated using a JEOL JSM-7001F-SEM, in secondary electron mode and operated at 2 keV. PIXE was used to map the elemental distribution, particularly Pt, on the surfaces of both the annealed (800 °C) and *in-situ* real time RBS analysed sample. A 3 MeV focused proton beam of about 3.5 μm × 3.5 μm lateral resolution was raster scanned on the sample surface (area of 20 μm × 20 μm) using an electrostatic scanning coil. Beam current was kept at about 100 pA with minimum instability in order to avoid sample damage. Scanned areas were typically analysed in a square pattern of up to a maximum of 28 × 28 pixels, with a dwell time of 10 ms/pixel. Spectra of PIXE coupled with a proton backscattering detector (at 176 °C scattering angle) were acquired in an event-by-event mode, using a Si (Li) X-ray detector positioned at an angle of 135° and shielded with a 125 μm Beryllium (Be) filter. The PIXE count rate was kept below 1000 counts/s to avoid pulse pile-up and to achieve satisfactory counting statistics. The accumulated PIXE spectra were analysed using GeoPIXE II software [10].

3. Results and discussion

Fig. 1 displays the *in-situ* real-time RBS results showing a colour coded plot of the total spectra collected from RT to 360 °C. During the temperature ramping process from RT up to ~220 °C, real time monitoring of the Pt-coated Si sample, indicates no reaction between Pt and Si (region 1). This can be attributed to the film being thermally stable in this temperature range. However, just above 220 °C (region 2), real-time RBS analysis indicates that Pt starts to react with Si to form a silicide phase. At 320 °C, the reaction between Pt and Si has reached completion and the formation of a stable silicide that existed up to the maximum temperature of the *in-situ* real-time RBS experiment was observed (region 5).

Fig. 2(a–d) shows the RBS experimental (dotted line) and simulated data (solid line) spectra extracted from Fig. 1 at four different annealing temperatures, RT, 230 °C, 300 °C and 350 °C. Two peaks of alpha particles backscattered from Si and Pt atoms can be seen at channels 275 and 470, respectively, Fig. 2(a). The surface channel position of Si is at 290, however with the energy loss in the Pt layer, the silicon signal appears at a 275 channel position. The peaks are clearly defined with no tails on either of the peaks and the thickness of the Pt film, from the simulation (solid line), was found to be 125 × 10^{15} atoms/cm^2 (~20 nm) in good agreement with the thickness set during deposition. The simulation of the spectra from RT up to about 220 °C gave similar results.

As shown in Fig. 1, the increase in temperature triggered the reaction between Si and Pt. Fig. 2(b–d) show spectra extracted at three critical temperature points (230 °C, 300 °C and 350 °C) and represent three stages of the Si and Pt reaction (the beginning (2), the continuation (3) and the final stage of the reaction (4)). In all spectra, a change in the Si and Pt peaks are noticeable, with a shoulder developing at the high energy side of the Si peak and a decrease of the yield at the lower energy side of the Pt peak. These changes are an indication of the interfacial reaction between Si and Pt which causes extra energy loss and thereby decreases the peak signal. The degree of change of the peak signal is linked to the amount of reacted Pt species i.e. the more the Pt atoms react with Si, the lower the signal on the lower energy side of the Pt peak and the higher the shoulder in the higher energy side of the Si peak as shown in Fig. 2(b–d). Furthermore, the simulation of spectra revealed the following:

i. At 230 °C, Pt had reacted with Si to form the silicide phase with stoichiometry 67 at.% Pt and 33 at.% Si (Pt_2Si), with a thickness 70 × 10^{15} atoms/cm^2 (Fig. 2(b)). At 260 °C, all Pt had fully converted into the Pt_2Si with a thickness 178 × 10^{15} atoms/cm^2 (region 2, Fig. 1).
ii. In region (3), the Pt_2Si phase was found to be stable from ~260 °C to ~290 °C before reacting with Si to form PtSi at about ~300 °C. Fig. 2(c) shows a simulation of a spectrum extracted at 300 °C, region (4) in Fig. 1, and it was found that Pt_2Si had reacted with Si to form another silicide phase with stoichiometry 50 at.% Pt and 50 at.% Si which corresponds to the PtSi phase. The spectrum was simulated with 97 × 10^{15} - atoms/cm^2 and 110 × 10^{15} atoms/cm^2, for Pt_2Si and PtSi, respectively. The existence of these two phases further increased the energy loss, and as a result the broadening of the Pt peak was observed.

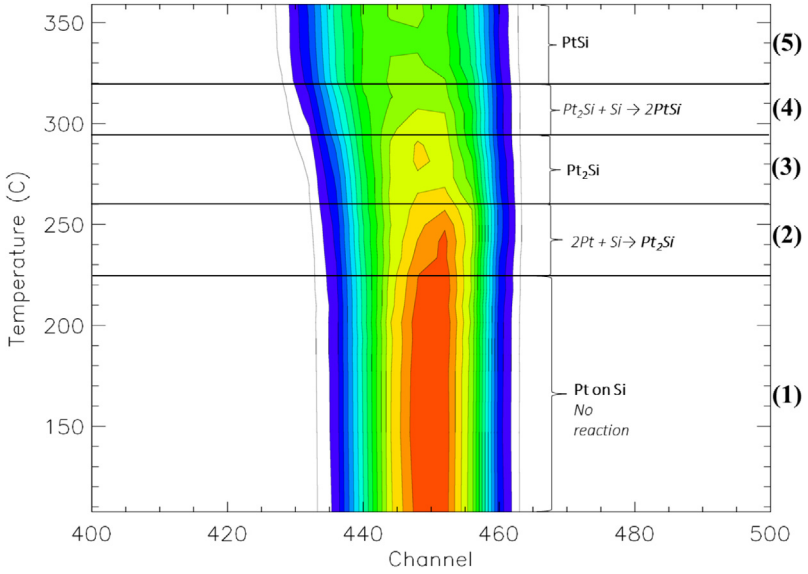

Fig. 1. In-situ real-time RBS results showing a colour coded plot of the total spectra collected from RT to 360 °C. Right vertical axis shows temperature regions (1–5) where particular phases are formed.

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