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Short communication

Plasma-plasmonics synergy in the Ga-catalyzed growth of Si-nanowires

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ABSTRACT

This paper reports on the growth of Si nanowires (NWs) by SiH_4/H_2 plasmas using the non-noble Ga-nanoparticles (NPs) catalysts. A comparative investigation of conventional Si-NWs vapour–liquid–solid (VLS) growth catalyzed by Au NPs is also reported. We investigate the use of a hydrogen plasma and of a SiH_4/H_2 plasma for removing Ga oxide shell and for enhancing the Si dissolution into the catalyst, respectively. By exploiting the Ga NPs surface plasmon resonance (SPR) sensitivity to their surface chemistry, the SPR characteristic of Ga NPs has been monitored by real time spectroscopic ellipsometry in order to control the hydrogen plasma/Ga NPs interaction and the involved processes (oxide removal and NPs dissolution by volatile gallium hydride). Using *in situ* laser reflectance interferometry the metal catalyzed Si NWs growth process has been investigated to find the effect of the plasma activation on the growth kinetics. The role of atomic hydrogen in the NWs growth mechanism and, in particular, in the SiH_4 dissolution into the catalysts, is discussed. We show that while Au catalysts because of the re-aggregation of NPs yields NWs that do not correspond to the original size of the Au NPs catalyst, the NWs grown by the Ga catalyst retains the diameter dictated by the size of the Ga NPs. Therefore, the advantage of Ga NPs as catalysts for controlling NWs diameter is demonstrated.

1. Introduction

Silicon nanowires (NWs) have received great interest due to their potential applications in nanoscale electronic [1], optoelectronic [2] and photovoltaic [3] devices. Specifically, the possibility to tailor NWs band gap and carrier transport properties by changing their size and doping, as well as their characteristic of high surface-to-volume ratio are promising for their applications in both inorganic and hybrid organic–inorganic solar cells [3], sensors [4] non-volatile memories [5], transistors [1], and phototransistors [2]. As an example of their potential, Si NWs electronic properties are appealing for post CMOS materials since p-type Si NWs with diameters of 20 nm have been recently shown to have a thermoelectric figure of merit of $ZT \approx 1$, whereas the bulk value is $ZT = 0.014$ [6].

Nevertheless, the use of Si NWs as building blocks for the future nanotechnology depends on the development of bottom-up approach for NWs growth, on large scale, directly on substrate of technological interest, with control over wire positioning, dimensions and directionality. Among the various methods developed for the NWs synthesis (laser ablation [7], molecular beam epitaxy (MBE) [8], solution growth [9]), lithography base techniques [10], the metal nanoparticles (NPs) catalyzed growth of nanowires from silicon gaseous precursors by the so-called vapor–liquid–solid (VLS) process [11] represents the most promising approach in terms of throughput, potential for high volume production and cost, especially when non-noble metal catalysts alternative to gold are used, because of the higher process rates compared to laser ablation and MBE and of the reduced process steps compared to nanolithography approaches.

So far, the vast majority of the work reported in the literature on the VLS methodology utilizes Au nanoparticles as the metal catalyst for the NWs growth from the silane (SiH_4) precursor. The choice of Au NPs as the metal catalyst is related to the favourable chemical and physical properties of this noble metal. In particular, Au is an efficient chemical catalyst for silane dehydrogenation/dissociation [12]. However, the use of gold as catalyst is undesirable because the Au diffusion into Si NWs leads to the creation of deep traps in the Si bandgap and, therefore, to the reduction of their carrier mobility [13]. Moreover, the high temperature required for thermal activation of the Au catalyzed VLS growth of NWs (in the range 500–950 °C [11,14]) is unfavourable for devices integration because it can cause substrate thermal damaging and enhance gold surface migration from the smaller droplets to the larger ones (Ostwald ripening), making difficult the NWs size and position control [15].

For these reasons, researchers have investigated low-melting metals such as, gallium (Ga) [14], indium [16], tin [17], and aluminium [18] as alternatives of gold. In particular, interesting results

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have been reported on the growth of Si NWs using gallium nanoparticles as catalyst [13,14]. Compared to gold, gallium offers the advantage of a low melting point of 29.8 °C, which is also the eutectic temperature for the Si/Ga binary system. This allows, potentially, the synthesis of nanowires at very low temperature and, therefore, the drastic reduction of production cost, together with their possible direct growth on plastic substrates. In addition, the low solubility of gallium in silicon can reduce the creation of traps in Si NWs through avoiding metal incorporation into NWs.

Since gallium is not known as a catalyst for silane dehydrogenation reaction, a significant difference of the Ga catalyzed Si NWs growth with respect to the Au catalyzed one is that a plasma source is needed to dissociate the silane (SiH_4) precursor to dissolve silicon into the metal catalyst [19]. Moreover, gallium, unlike gold, is not a noble metal. Therefore, an oxide coating forms on the Ga catalyst surface owing to air exposure [20]. This oxide shell can inhibit the silicon dissolution on the catalyst surface and avoid the NWs growth. Although a hydrogen plasma treatment of the Ga NPs catalyst for oxide removal has been reported [13], a systematic study on the Ga NPs/atomic hydrogen interaction and on its effect on the catalyst and on the resulting NWs growth mode is still lacking.

In this article we provide a comparative investigation of Ga and Au catalyzed VLS growth of Si NWs. We use *in situ* spectroscopic ellipsometry (SE) and laser reflection interferometry (LRI) as optical diagnostic techniques for the process monitoring of both the catalyst pretreatment and the NWs growth. We take advantage of surface plasmon resonance sensitivity to Ga NPs surface chemistry and morphology [13] to investigate the process chemistry of Ga NPs hydrogen plasma treatment. The Si NWs growth process is investigated by *in situ* LRI [21]. The comparative investigation of the NWs growth kinetics exploiting the two different metals catalysts is carried out to find the role of the SiH_4 plasma activation in the case of the Ga catalyzed NWs growth. Furthermore, the role of atomic hydrogen in the NWs growth mechanism and, specifically, in the silane radicals dissolution into the catalysts, is found, leading to the understanding and the control of the NWs growth by catalysts alternative to gold.

2. Experimental

For the Ga catalyzed plasma enhanced (PE)-VLS growth of silicon nanowires, Ga nanoparticles (diameter ranging from 100 to 500 nm) were prepared at room temperature on SiC substrate using Ga cell of molecular beam epitaxy system. The Ga NPs size was determined by the Ga flux and the deposition time. Details on the NPs deposition experimental set-up have been previously reported in [22]. Ga NPs oxidation by air exposure was confirmed by *ex situ* X-ray photoelectron spectroscopy (XPS) measurements indicating the presence of Ga_2O_3 bonds in Fig. 1b. Conversely, the XPS of Au NPs (Fig. 1a) only shows the metallic Au 4f level (only one fit component with a full with at half maximum of 0.6 eV). In order to remove this oxide overlayer and activate Si NWs growth, Ga NPs were pretreated at 500 °C with an rf (13.56 MHz) hydrogen plasma operated at 4 W and at a pressure of 0.1 mbar for 500–2000 s. NWs were grown by using a SiH_4 (10% diluted in H_2) rf (13.56 MHz) plasma operated at 4 W and at a SiH_4 partial pressure of 0.15 mbar. The growth was carried out at 550 °C for 800 s.

For the Au catalyzed VLS growth of silicon nanowires, Au NPs (diameters ranging from 20 to 35 nm) were grown by sputtering of an Au target using an rf (13.56 MHz) Ar plasma (14 W and 0.3 mbar) (see Ref. [23]). The size of the Au NPs is limited by the sputtering methodology, since by increasing the sputtering time, which is the parameter used to tailor the Au NPs size, and therefore the Au amount, coalescence of NPs into a film is achieved. This gives a reason why Au NPs of a diameter of approximately 20 nm were used in the present study. On the other hand, this limitation does not exist in the case of thermal evaporation of Ga NPs, since Ga is liquid at room temperature and hemispherical droplets of any size form. Therefore, larger Ga NPs were used to show the possibility to deposit larger diameter NWs, taking advantage of the larger Ga NPs size.

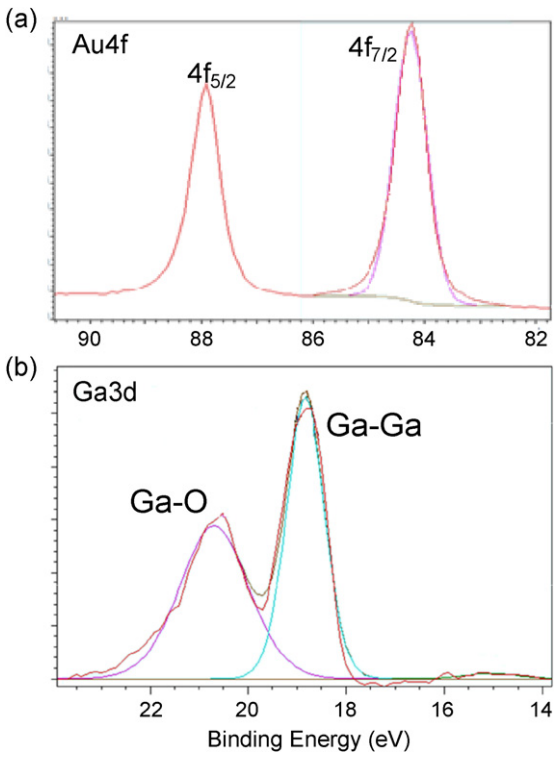

Fig. 1. X-ray photoelectron spectroscopy (XPS) spectra of the Au4f (a) and Ga3d (b) photoelectron core levels for the Au NPs and Ga NPs after air exposure. The peaks expected for metallic Ga and Ga-O are also shown.

Nanoparticles were formed by deposition of 40 Au monolayers (MLs) on Si (1 1 1) at room temperature and subsequent annealing at 600 °C for 1200 s in UHV. The Au catalyzed VLS growth of silicon nanowires was carried out for 2500 s at 600 °C and with a SiH_4 partial pressure of 0.15 mbar.

NPs catalysts optical characterization was performed through exploiting spectroscopic ellipsometry (SE). The pseudodielectric function, $\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + i\langle\varepsilon_2\rangle$, was observed in the range 0.75–6.5 eV with a phase-modulated spectroscopic ellipsometer (UVISEL-Jobin Yvon) at an incidence angle of 70°. NWs growth process was monitored by laser reflectance interferometry using a 635 nm diode laser and a Si photodiode assembled on the plasma reactor at an angle, Φ, of 70° relative to the substrate surface. The 70° corresponds to the Brewster angle for Si defined as $\Phi = \arctan n$, where n is the refractive index of silicon.

Metal catalysts and NWs structural characterization were carried out by atomic force microscopy (AFM) and scanning electron microscopy (SEM).

3. Results and discussion

Fig. 2a shows the full plasmonic spectrum of oxidized Ga NPs in an extended spectra range where both the longitudinal (LO) and transverse (TO) plasmon modes are shown. Since the *in situ* ellipsometry system works in a narrower spectral range (1.5–5.5 eV), we followed the de-oxidation kinetics on the TO plasmon mode as shown in Fig. 2b. Fig. 2b shows the time evolution of $\langle\varepsilon_2\rangle$ of the Ga nanoparticles during the hydrogen plasma treatment for the oxide