SiGe/Si Nanowire Axial Heterostructures Grown by LPCVD Using Ga-Au

A. Rodríguez[1], T. Rodríguez[1], C. Ballesteros[2], J. Jiménez[3]
[1] Tecnología Electrónica, Universidad Politécnica de Madrid, E.T.S.I.T., 28040 Madrid, Spain
[2] Física, Universidad Carlos III, 28911 Leganés (Madrid), Spain
[3] GdS Optronlab, Ed. I+D, Universidad de Valladolid, 47011 Valladolid, Spain

ABSTRACT

The use of Ga-Au alloys of different compositions as metal catalysts for the growth of abrupt SiGe/Si nanowire axial heterostructures has been investigated. The heterostructures grown in a continuous process by just switching the gas precursors, show uniform nanowire diameters, almost abrupt compositional changes and no defects between the different sections. These features represent significant improvements over the results obtained using pure Au.

INTRODUCTION

Axial SiGe-based nanowire (NW) heterostructures (HE) and superlattices are attractive for the design of advanced devices with potential applications in nanoelectronics; besides, their growth process may be compatible with current device fabrication technologies [1]. The most commonly used catalyst metal for the growth of semiconductor NWs by the Vapour-Liquid-Solid (VLS) method is Au. This method combined with Chemical Vapour Deposition (CVD) techniques has been successfully used to grow Si and SiGe NWs of different compositions. In principle, axial SiGe/Si NW HEs are easy to produce using this process by just switching the gas precursors. However, an important feature of the Au-Si and Au-Ge binary phase diagrams is the high atomic concentration of Si or Ge in the liquid at the usual growth temperatures [2]. If a SiGe/Si HE is being grown and the composition of the precursor gas is changed, the Ge still dissolved in the metal has to be diluted out of the droplet to get a pure Si nanowire segment. Considering that several full droplet fillings are required to get the dissolved Ge out of the droplet, the result will be a compositionally graded junction. It has been shown that this is indeed the case, and also that the length of the transition region scales with the nanowire diameter [3].

The VLS growth of Si NWs using other metals, like Ga or In has been considered [4, 5]. These metals show very low solubilities of Si and Ge, an effect that could be advantageous to improve the abruptness of interfaces in Ge/Si and SiGe/Si NW HEs [2]. However, they are not catalytic, so conventional CVD cannot be used and plasma assisted CVD techniques are required [4-6]. The use of alloys of catalytic and non-catalytic metals, like Ga-Au, appears as an alternative to take advantage of the properties of both species using a conventional CVD process. Ga-Au alloys have been used already for the growth of high quality Si NWs by CVD [7]. Cylindrical and straight SiGe NWs of good crystalline quality and an almost constant composition have also been grown by Low Pressure CVD (LPCVD) using Ga-Au alloys [8]. In this last case, it has also been shown that the interfaces between the NW and the metal droplet are sharper than those obtained using pure Au, which points to the possibility of the formation of high quality HEs with flat and sharp interfaces.

The growth of SiGe/Si nanowire axial heterostructures using LPCVD and different Ga-Au alloy droplets is investigated in this work, with emphasis on the study of the compositional abruptness and the crystalline structure of the interfaces. These features are compared with those of the HEs grown in the same conditions using pure Au droplets as catalysts.

EXPERIMENTAL

SiGe/Si axial NW HEs were grown by the VLS method using a commercial LPCVD reactor designed for the processing of Si wafers four inches in diameter, Si_2H_6 and GeH_4 as precursor gases for Si and Ge respectively and Ga-Au metallizations of different compositions as catalysts.

Thermally oxidized Si wafers were used as substrates and metal films of Ga and Au were deposited on top of them by thermal evaporation (Ga was always evaporated first). The Ga content was varied by changing the expected thickness to be achieved from each evaporation process and keeping the total thickness of around 10 nm. The values of the nominal Ga content were 0% (pure Au), 50%, 75% and 90%. Pure Ga was not used since it is not catalytic and no NW growth is produced using this LPCVD reactor, the presence of some amount of Au in the metal being necessary due to its catalytic properties [4, 5]. Prior to every growth run, the samples were annealed at 500 °C in H_2 atmosphere inside the LPCVD reactor to form the metal droplets.

In previous studies, single Si NWs were grown at 470 °C using Si_2H_6 while SiGe NWs with a Ge atomic fraction of 0.1 were grown at 430 °C using a GeH_4:Si_2H_6 gas flow ratio of 1. In both cases H_2 was the carrier gas and the total pressure was 400 mTorr [8]. The density of Si and SiGe NWs grown in these conditions was similar, the diameters were always in the 30-50 nm range and both types of NWs exhibited good crystalline quality. The lattice mismatch between these Si and SiGe NWs is small, and therefore it would be easily accommodated by strain in a HE formed by sections of both materials. Different approaches were considered to achieve a good matching between the SiGe and Si NW segments of the HEs, which will be described later on.

The grown HEs were separated from the substrate by sonication of the samples and collected in a methanol bath. Transmission Electron Microscopy (TEM) was used for the characterization of the HEs. Compositional studies were carried out in Z-contrast Scanning TEM (STEM) mode using an Energy Dispersive X-ray Emission (EDX) system attached to the microscope. Si and Ge compositional maps were obtained using the intensities of the Si K_α and Ge K_α X-ray lines respectively to study the NW composition across the HE interface. High resolution TEM images were taken to analyze the crystalline structure and possible defects at the interfaces.

RESULTS

HE growth approaches

The first approach considered consists of the growth of the first segment, of either SiGe or of Si, using the corresponding processing conditions, then the stop of the precursor gas flow followed by the fast evacuation of the precursor gases inside the reactor using the system pump to stop the growth as abruptly as possible, and the subsequent modification of the temperature and gas composition to grow the second section (of Si or of SiGe respectively). The second approach considered also consists of stopping the growth of the first section to readjust the

conditions for the growth of the second section but, instead of evacuating the chamber once the precursor gas flow is stopped, the H_2 carrier gas flow and the total pressure inside the chamber were increased up to the limits of the system in an attempt to dilute the residual gases still present and drift them out of the reactor in a time as short as possible. Both approaches resulted in anomalous SiGe/Si junctions with changes in growth direction, local increase in diameter by the accumulation of material and lateral growth of thin whiskers, so the growth stop stage was investigated in detail by growing single SiGe NWs and analyzing the region next to the droplet.

In the first case, Figure 1-a, it is found that the fast evacuation of the chamber was catastrophic for the integrity of the liquid droplet, which in most cases is split out in a main droplet and several smaller ones that give rise to the growth of a main NW section and several secondary NWs of smaller diameters from the residual gas still present in the reactor. The composition of the additional main segment and the small whiskers was found by high resolution TEM to be pure Si with wurtzite structure, although the preceding NW segment was SiGe. In the second case, see Figure 1-b, the region of the single SiGe NW located near the droplet appears decorated with Au small drops due to unwanted Au diffusion on the NW sidewalls during the growth stop stage of the process [9]. Growth continues further from the main droplet due to the presence of residual gases inside the chamber, in most cases in the same direction than the preceding NW segment, being this additional section also pure Si with wurtzite structure.
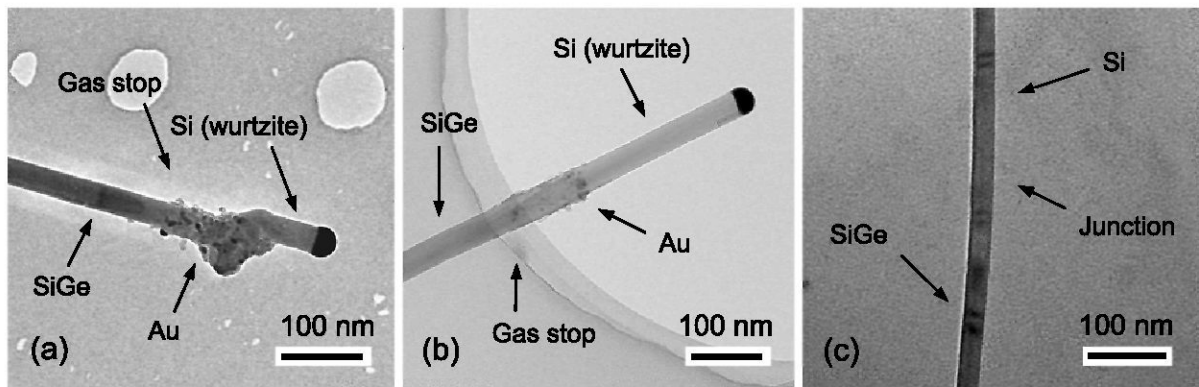

Figure 1. TEM images of SiGe single NWs grown at 430 °C using Ga-Au with 75% Ga and a precursor gas flow ratio of 1 with gas flow removal and subsequent (a) evacuation of the chamber or (b) increase in H_2 flow and total pressure. TEM image of a SiGe/Si heterostructure grown in a continuous process at a constant temperature of 430 °C by switching the precursor gas composition and using a metallization with 90% of Ga (c).

Once both approaches were discarded, a third approach consisting of a continuous growth process was considered. In this case, a SiGe or Si segment is grown and the composition of the precursor gas mixture is just switched after a certain growth time to the one necessary for the subsequent growth of Si or SiGe, but the growth is not stopped and the total pressure and temperature remain unchanged. The successful growth of HEs was achieved either by growing first a Si segment and then a SiGe segment at a constant temperature of 470 °C, or by growing the two segments in opposite sequence at 430 °C, in both cases with a total process time of 10 minutes. However, it has been found that if Si is grown first and SiGe is grown then, the Si segment appears covered by a thin layer of Ge, which is clearly evidenced in the transversal composition profiles obtained by EDX (not shown here), thus making more difficult the study of the composition of the HE in the transition region since Ge is present at both sides of the

junction. For this reason, the HEs grown for this study were of the SiGe/Si type, in such way that the possible presence of Ge in the second section can only be due to the existence of a compositionally graded junction. So, the effect of the Ga-Au catalyst on the abruptness of the composition change can be analyzed and compared to that resulting from the use of pure Au. It is remarkable that the growth of Si proceeds at 430 °C once SiGe has been grown, while the same process starting from the droplets located at the substrate would have resulted in the growth of a small density of Si NWs or even no growth at all. An example of one of these HEs is shown in the TEM image of Figure 1-c, where no changes at all in diameter, growth direction or contrast are appreciated; furthermore, the outer surface of the NWs appears clean and with no protuberances or spots in the junction region.

Compositional analysis

Figure 2 shows STEM images of the surroundings of the SiGe/Si interfaces of several NW HEs grown using the continuous process but with different Ga contents in the metal droplets. Intensity maps of the Si K_α and Ge K_α X-ray lines obtained by EDX are shown in each case.

The Z-contrast STEM images don't reveal the presence of a junction in the NWs, in agreement with the TEM micrographs. EDX maps of the Si K_α line show that Si is present and almost homogeneously distributed all along the NW length. No significant changes in the intensity of this line are detected along the NWs, probably because the Si atomic content is around 0.9 in the SiGe sections and 1 in the Si ones. However, the Ge K_α X-ray line maps reveal that Ge is clearly present and detected in one part of the NW and fully absent in the other one. The intensity of the Ge K_α X-ray line in a direction perpendicular to the NW main axis is also included in Figure 2 to show that Ge is unambiguously detected in the SiGe sections of the HEs.

The EDX analysis of the droplets located at the end of the NWs shows that they contain Ga once the growth is completed. The influence of the presence of Ga in the metal droplets is therefore clear and evidenced in these images. In the HEs grown using Au, the intensity of the Ge K_α X-ray line decreases gradually and finally vanishes. Therefore, the Ge content along this part of the NW is graded and the length of the transition region is several times the NW diameter. However, the intensity of this line, and correspondingly the Ge content in the NW, completely vanishes within a distance smaller than the NW diameter if Ga is present in the metal droplet. With regard to the influence of the amount of Ga in the droplet on the length of this transition region, no remarkable differences are observed between the HEs grown using metal alloys with 50% or 90% of Ga. In both cases the abruptness of the Ge content change is similar and significantly different from the one observed in HEs grown using pure Au; therefore, the role of Ga as a metal with low Ge solubility in the improvement of the HE is clearly revealed.

The total amount of Ge that can be dissolved in the droplet depends on its diameter, so there is a correlation between the diameter of the NW and the length of the transition region that could mask the effect of Ga on the compositional abruptness of the interface. This possible effect is eliminated from the study since the EDX maps of the HEs grown using Au and Ga-Au with 90% of Ga shown in Figure 2-a and 2-d correspond to NWs of exactly the same diameter, 32 nm, while the graded region is very long in the former case and almost inexistent in the latter one.

Considering that the complete change in the composition of the precursor gases in the large reactor chamber of this LPCVD system exclusively by drift takes a time which is not negligible compared to the growth time, it seems that the abruptness of the compositional change could be improved if, in addition to the use of Ga-Au, the HE growth is carried out in a smaller reactor.
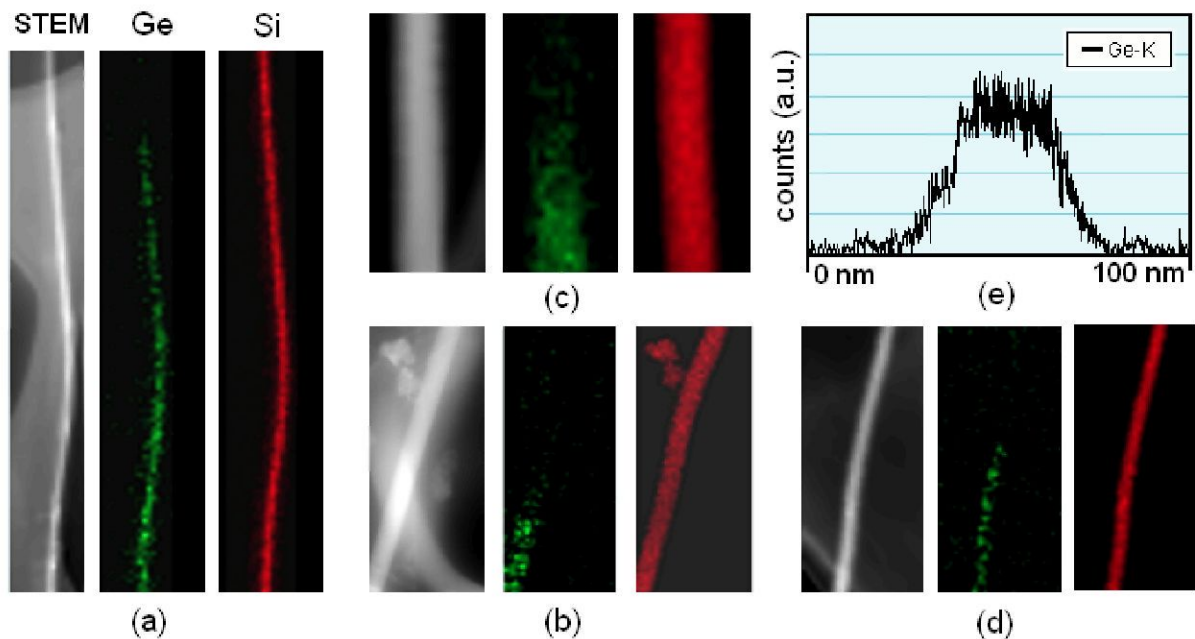
Figure 2. Z-contrast STEM images and EDX compositional maps obtained using the Si K_α and Ge K_α X-ray lines of SiGe/Si nanowire heterostructures grown with Ga-Au metal droplets of pure Au (a), 50% Ga (b, c) and 90% Ga (d). A typical Ge K_α X-ray line intensity profile recorded in a direction transversal to the main NW axis in the SiGe section of the HE is shown in (e). The diameters are 32 nm (a), 43 nm (b), 47 nm (c) and 32 nm (d).

Structural analysis

Figure 3 (a) shows high resolution TEM images of SiGe/Si HEs. The crystalline structure is diamond-like all along the HE and it is not possible to identify any discontinuity or interface in the images. No distortions, stacking faults or other defects are visible in the image of the left side, while it is unclear if there are some defects in the one displayed on the right side.
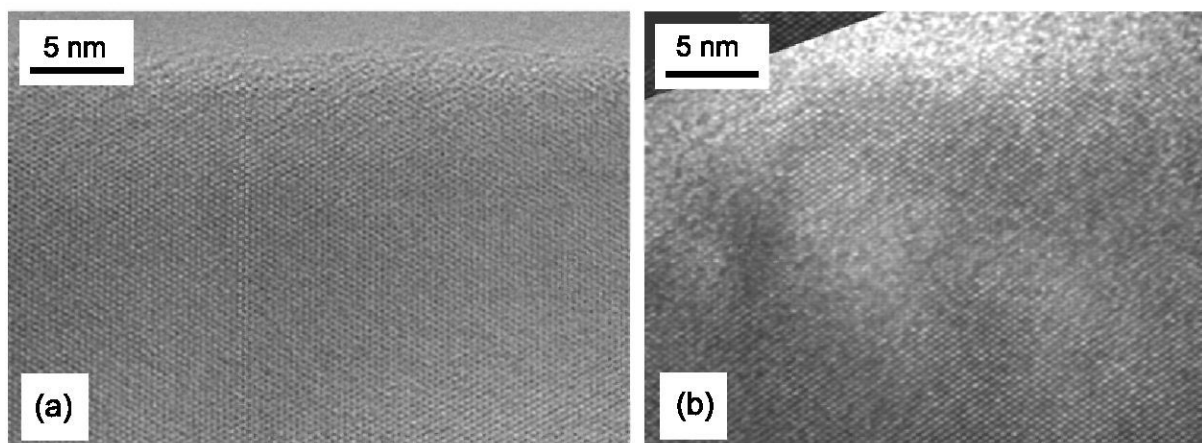

Figure 3. High resolution TEM micrographs of SiGe/Si NW HEs grown at 430°C using Ga-Au with 50% Ga (a) and 75% Ga (b). The images correspond to the region where the transition region of the junction is located. The main axis of the NW is horizontal and the SiGe sections are located on the left side in both cases.

CONCLUSIONS

SiGe/Si nanowire heterostructures have been grown by the VLS method using Ga-Au metal films with of different compositions and a standard and commercial LPCVD reactor. The growth was carried out in a continuous process at constant temperature and pressure just by switching the precursor gas composition from a mixture of GeH_4 and Si_2H_6 to pure Si_2H_6. The abruptness of the composition change from the SiGe section to the Si one is clearly improved if Ga-Au instead of pure Au droplets are used, due to the low solubilities of Ge and Si in Ga compared to those in Au. It could be further improved if a reactor with a small process chamber, in which a fast evacuation of the residual gas by drift after the growth of the first section of the HE can be achieved, is used instead the commercial one designed for the processing of four inches wafers. No protuberances, spots, changes in diameter or growth direction, defects, dislocations or stacking faults are observed in low and high resolution TEM images taken of the interfaces.

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