GaAs nanowires by Mn-catalysed molecular beam epitaxy

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Abstract. GaAs nanowires were synthesized by molecular beam epitaxy on different substrates using Mn as catalyst. High density of 1D nanowires was obtained at growth temperature between 540 and 620 °C on SiO₂ substrates. On oxidised GaAs substrates nanowires grow together with 2D nanostructures that are dominant. Nearly no nanowires were instead obtained on epitaxial GaAs. The nanowire yield on the different substrates is correlated to the chemical reactions taking place between substrate and catalyst before the growth, as detected by x-ray photoelectron spectroscopy.

1. Introduction
Self aggregated semiconductor nanowires (NWs) [1] are attracting great interest for their potential applications in electronics and optoelectronics at nanoscale, as well as for the physics underlying their growth mechanism. NWs are obtained by a number of growth techniques and one dimensional (1D) growth is generally assisted by the presence of a metal catalyst particle. Gold is the most commonly used catalyst. Diffusion of gold inside the NWs has been reported [2,3]. This feature might be detrimental for the electronic properties of the wires, especially in case of silicon NWs.

On the other hand the catalyst diffusion into the nanowires can be exploited to change in a controlled way the electronic properties of the NWs. The fabrication of GaAs NWs by molecular beam epitaxy (MBE) has recently been obtained by using Mn as the growth catalyst [4]. This could be the first step toward the fabrication of GaAs:Mn NWs and would open the possibility to develop 1D ferromagnetic semiconductors to be integrated with the GaAs technology. In the present paper we show in particular that the catalyst Mn produces different NW yields using different substrates and we discuss the role of the presence of oxygen on the substrate surface on the growth of the NWs.

2. Experimental
NWs were grown in a facility including a MBE growth chamber for III-As compounds, a metallization chamber for Mn deposition and an analysis chamber for x-ray photoelectron spectroscopy (XPS), all interconnected in ultra high vacuum (UHV).

Different substrates were used: Si wafers covered by 200 nm of thermally grown SiO₂ (in the following simply SiO₂), commercial GaAs (001) wafers (in the following ox-GaAs), where GaAs surface is protected by an oxide layer few tenth of nm-thick [5], and fresh epitaxially grown GaAs (in the following GaAs), both (001) and (111)B oriented.

The epitaxial GaAs was grown by standard MBE procedures on GaAs substrates, while SiO₂ and ox-GaAs were first heated in UHV for 30’ at 300 °C, to degas atmospheric contaminants. After the first treatment all substrates were transferred in the metallization chamber, where 1 nm of manganese
was deposited at room temperature. The substrates were then introduced in the MBE chamber and GaAs growth was performed for 30’ at substrate temperatures in the 500–650 °C range, using Ga and As effusion sources in growth conditions corresponding to a 2-D growth rate of 1 μ/h. The results of the growth were analyzed by scanning electron microscopy (SEM) using a ZEISS Gemini microscope, equipped with a field emission gun. In separate experiments few substrates were transferred to the XPS analysis chamber at different stages of the process before the growth of NWs, in order to get information about the chemistry of the substrate surface and the state of the catalyst.

3. Results
In figure 1 we show representative SEM images of the NW yield obtained at selected growth temperatures (510, 540, 600 and 650 °C, respectively) on SiO₂ substrate. At growth temperatures (T_g) between 540 and 620 °C (figures 1(b) and 1(c)) we obtain a high density of several μ-long NWs, with lateral dimension between tens and 200 nm, often slightly tapered. In this temperature range little differences are observed. Together with the NWs, few quasi-2D structures, a kind of nanoleaves, are also obtained. At temperatures lower than 540 °C only rare and short nanostructures are observed after the growth process (see figure 1(a)). At T_g = 650 °C almost no structures has grown (figure 1(d)).

![Figure 1. Mn-catalysed NWs deposited on SiO2 at different temperatures: (a) 510 °C, (b) 540 °C, (c) 600 °C, (d) 650 °C.](image)

In figure 2 we show representative SEM images of NWs synthesized on (100) ox-GaAs substrates for growth temperatures of 510, 540, 600 and 650 °C, respectively. Between 510 and 620 °C we observe the coexistence of NWs and nanoleaves, with the amount of the latter higher than observed on SiO₂. The nanoleave density increases with increasing substrate temperature, and becomes predominant above 560 °C. Both kinds of nanostructures appear to be somehow ordered on the substrate surface.

Compared with the NWs grown on SiO₂, the NWs obtained on ox-GaAs seem to be shorter and with irregular shape. Optimal growth temperature to maximize the amount of wires compared with leaves is around 540 °C. Similarly to what found on SiO₂, at 650 °C very rare nanostructures are found on ox-GaAs.

Nanowires growth was also observed on the GaAs (110) surface obtained by cleaving in air a (001) GaAs commercial wafer right before its introduction into the UHV system. A SEM image for wires grown on this latter surface at 540 °C is shown in figure 3.
Figure 2. Mn-catalysed NWs deposited on ox-GaAs at different temperatures: (a) 510 °C, (b) 540 °C, (c) 600 °C, (c) 650 °C.

Figure 3. Mn-catalysed NWs grown on (110) GaAs surface obtained by cleavage in air of a GaAs (100) substrate.

More difficult appears to be the growth of NWs on GaAs epitaxial substrates, as shown in figure 4. On (100) GaAs only rare, short and irregular 1D nanostructures are found at low substrate temperature (540 °C) [Figure 4(a)]. By rising the temperature the nanostructures become even rarer (not shown). Similarly, nearly complete absence of nanowires is observed on epitaxial (111) GaAs [figure 4(b)].

An abundant yield of NWs can however be obtained on both epitaxial (100) and (111) GaAs if, after the catalyst and before the GaAs deposition, the substrate is exposed to a residual atmospheric pressure of 3 $10^{-7}$ torr for 30’. Representative SEM images of the NWs obtained at $T_g = 540$ °C with this process on the (100) and (111) surfaces are shown in figure 4(c) and (d), respectively. These results suggest that the substrate surface plays an important role in the growth of the NWs, and more specifically that the presence of oxides is determinant for the synthesis of Mn-catalysed nanostructures by MBE.

In order to check this hypothesis and to get insight about the origin of the differences in yield and morphology observed for NWs grown on different substrates, we have investigated by XPS the substrates surface before and after the deposition of the catalyst layer, and after heating the substrate+ catalyst system in the growth chamber at 540 °C for 10’. This temperature was chosen because it allows the growth of good quality NWs on both ox-GaAs and SiO$_2$, but gives no wires on epitaxial GaAs.
Figure 4. NW synthesised on: (a, b) epitaxial (100) and (111) GaAs surface, respectively. (c, d) epitaxial (100) and (111) GaAs, respectively, after oxidation of the catalyst as described in the text.

In figure 5 (a, b and c) we show the photoemission intensity, recorded in the binding energy region corresponding to Mn 3p and As 3d core-level emission, as obtained on the clean substrates (bottom traces), after deposition of 1 nm of Mn (middle traces) and after heating at 540 °C (top traces) for SiO2, ox-GaAs and (001) GaAs, respectively.

In case of SiO2 (figure 5(a)), the Mn 3p core-level asymmetric line-shape of the as-deposited Mn layer is typical of a metal [6]. After heating, a high binding energy component in the Mn 3p core level emission becomes evident, corresponding to partial oxidation of the metallic layer.

Figure 5: XPS spectra recorded on the clean substrates (bottom traces), after deposition of 1 nm of Mn (middle traces) and after heating at 540 °C (top traces) for SiO2 (a), ox-GaAs (b) and (001) epitaxial GaAs (c).
A very similar spectrum, with both a metallic and an oxide Mn $3p$ component was recorded after heating at 600 °C (not shown).

Different behaviour has been instead observed on ox-GaAs (figure 5(b)). The photoelectron spectrum of the substrate surface before the deposition of the catalyst is characterized by the features corresponding to As 3d core level in GaAs (at 41.5 eV), and in the surface oxides compounds As$_2$O$_3$ and As$_2$O$_5$ (between 44 and 47 eV)[7]. The as-deposited Mn layer in figure 5(b) displays a Mn $3p$ emission overall shifted to higher binding energy, with a complex fine structure, characteristic of Mn in oxidized state [8]. We note that the deposition of Mn also involves the nearly complete disappearance of the emissions corresponding to the As oxides, suggesting that Mn oxidation takes place by reduction of the As oxides. By heating the substrate no substantial change can be detected in the Mn $3p$ line-shape, while a further reduction of the emission intensity of As oxides is observed. The same experiment performed on epitaxial GaAs(001) (figure 5(c)) reveals that the metallic Mn$3p$ emission recorded on the as-deposited Mn layer nearly disappears by heating the substrate at 540 °C, pointing out a dramatic reduction of the thickness of the Mn layer.

4. Discussion and conclusions

Different chemical reactions take place on the different substrates after depositing manganese and heating the system at the growth temperature before starting the GaAs deposition. The metallic Mn layer deposited on SiO$_2$ undergoes partial oxidation. Differently, complete oxidation takes place on ox-GaAs, at least within the detection limit of our XPS. The absence of oxygen on the epitaxial GaAs surface prevents the formation of Mn oxides and, when the substrate is heated, Mn is desorbed from the GaAs surface or possibly diffuses inwards the GaAs substrate.

The abundant yield of good quality NWs obtained on SiO$_2$ corresponds to the presence of both metallic and oxidized Mn. The higher density of nanoleaves observed on ox-GaAs seems to be related to the nearly complete oxidation of Mn, that on that substrates takes place already at room temperature. On the other hand, the absence of nanostructure observed on epitaxial GaAs can be ascribed to the nearly complete absence of manganese on the substrate at growth temperature.

In conclusion we have demonstrated that a high density of GaAs nanowires can be obtained by MBE using Mn as growth catalyst. This result opens a way to reach the fabrication of 1D dilute magnetic semiconductors. The investigation of the first steps of the growth process indicates that the presence of oxygen seems to be determinant in stabilizing the catalyst on the surface and therefore allowing the growth of Mn catalysed nanostructures.

References

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