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Au-assisted growth of GaAs nanowires by gas source molecular beam epitaxy: Tapering, sidewall faceting and crystal structure

M.C. Plante, R.R. LaPierre*

Department of Engineering Physics, Centre for Emerging Device Technologies, McMaster University, Hamilton, Ont., Canada L8S 4L7

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Abstract

GaAs nanowires grown by gas source molecular beam epitaxy for 3, 10, 30, and 40 min durations were studied by both scanning and transmission electron microscopy, providing a description of the time evolution of the nanowire morphology and structure. Tapered, "pencil-shaped" wires were observed in which a transformation of the sidewall orientation occurs from $\{\bar{1}\,1\,0\,0\}$ facets at the tip to $\{\bar{2}\,1\,1\,0\}$ facets at the base, providing evidence for a layer-by-layer radial growth model. The crystal structure of the nanowires, as well as the nature and frequency of stacking faults, was investigated. Local pseudo-periodicity of defects was observed in the vicinity of the wire base, while defect density decreased as the growth progressed.

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1. Introduction

While various methods exist to synthesize semiconductor nanowires (NWs) [1], the bottom-up approach in which the crystal grows from a metal seed particle has certainly attracted the most attention over the past 10–15 years. This process, where the size of the metal particle determines the diameter of the crystal, was first reported by Wagner and Ellis more than 40 years ago to explain the epitaxial growth of micron-sized Si whiskers [2]. These authors described the growth according to a vapor–liquid–solid (VLS) mechanism, in which a liquid droplet consisting of an alloy of the metal and growth species (supplied by the surrounding vapor) promotes the nucleation and growth of a crystal at the liquid–substrate interface. Interest in this mechanism was again generated in the early 1990s, when Hiruma et al. [3] demonstrated its applicability at the nanometer scale to fabricate the first III–V NWs.

The downscaling in the size of crystals that can be synthesized further opens the door to the development of devices that were not possible in two-dimensional (2D) epitaxial growth, such as highly mismatched heterostructures incorporated in the NWs [4,5]. Moreover, monolithic integration of III–V structures on group IV substrates [6,7] now becomes a viable path not only for performance enhancement of existing devices, but also incorporation of new functionalities. As a result, it is now well recognized within the research community and the semiconductor industry (see for instance the International Technology Roadmap for Semiconductors [8]) that 1D structures will play a major role in the efforts towards device miniaturization and the development of novel applications. Already, semiconductor NWs have demonstrated their potential in a wide range of electronic, photonic, and sensing devices [9–13].

Despite these tremendous achievements, the details surrounding the exact nature of the mechanisms involved

*Corresponding author. Tel.: +1 905 525 9140x27764; fax: +1 905 527 8409.
E-mail address: lapierr@mcmaster.ca (R.R. LaPierre).

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during NW growth are still not fully understood, and are the subject of numerous investigations. These efforts are essential in the determination of the optimum deposition conditions that will yield predictable and consistent structures (e.g. core–shell vs. axial heterostructures). The majority of studies reported in the literature of III–V NWs discuss the growth by either metal-organic vapor phase epitaxy (MOVPE) or chemical beam epitaxy (CBE). The deposition by molecular beam epitaxy (MBE) remains in comparison at a fairly early stage. This technique offers great potential for the fabrication of structures with very abrupt interfaces within a single NW, as recent results obtained with the analogous CBE method demonstrated [14].

In this paper, we present the morphology and evolution of GaAs NWs grown from Au seed particles by gas source molecular beam epitaxy (GS-MBE). The crystalline structure, the onset of radial growth, and tapering are discussed. In addition, we elaborate a qualitative growth model that we previously presented [15].

2. Experimental details

Si-doped (carrier concentration $1.6–2.3\times10^{18}\,cm^{-3}$) (1 1 1) B-oriented GaAs substrates (AXT Inc. [16]) were first submitted to a UV–ozone cleaning treatment in order to remove any hydrocarbon contamination. The resulting protective oxide layer was etched by dipping the substrates in a commercial 10% buffered HF solution for 30 s, and subsequently rinsing under flowing deionized water for 10 min. Following the surface preparation, the substrates were then immediately transported in ambient air to an e-beam evaporator system to deposit a 4-nm-thick film (as measured by a quartz crystal monitor) of Au at room temperature. For the synthesis of Au nanoparticles and growth of NWs, the substrates were transferred to a GS-MBE system (SVT Associates Inc. [17]), in which group III species are supplied as monomers from a heated solid elemental source, and group V species are supplied as dimers (As_2) from a hydride (AsH_3) gas cracker operating at 950 °C. The substrates were initially degassed for 15 min at a temperature of 300 °C. In the growth chamber, oxides were desorbed by heating the substrates to a temperature of 525 °C while submitting them to a hydrogen plasma from an inductively coupled plasma source for 10 min under an As_2 flux. The heat treatments give rise to the formation of nanoparticles on the surface [18]. Growth of NWs was initiated by opening the Ga shutter (atom flux yielding a 2D growth rate of 1 ML (monolayer)/s), with the As_2 flux set to a nominal V/III ratio of ~1.5, and the substrate temperature kept at a constant value of 525 °C. These conditions were maintained for durations of 3, 10, 30, and 40 min in four separate growths, after which the substrates were cooled under the As_2 flux, and brought back to ambient conditions.

Characterization of the resulting NWs was performed using a JEOL JSM-7000F field emission scanning electron microscope (FE-SEM) operated at 5 kV (for tilted views) and 15 kV (for top views) in the secondary electron mode to obtain information on surface density (number of NWs per unit area) and morphology (growth orientation on the substrate, height, faceting orientation). Crystal structure was investigated using a Philips CM12 conventional transmission electron microscope (CTEM) operated at 120 kV for bright-field imaging and selected area electron diffraction (SAED), while a JEOL JEM-2010F high-resolution TEM (HR-TEM) operated at 200 kV was used for lattice resolved imaging. For the TEM analysis, the NWs were broken off the surface of the substrates by putting a specimen in a vial, adding acetone, and sonicating for 1–2 min. A small volume (~20 μl) of the solution was then pipetted onto a standard TEM copper carbon holey grid, resulting in NWs being dispersed after solvent evaporation.

3. Results

The specimens were first characterized by SEM and CTEM in order to determine the morphology of the NWs. Typical tilted views of the surfaces after a 3-, 10-, and 30-min growth are shown in Fig. 1a–c, along with TEM images of representative NWs from each specimen as insets. In the case of the 40-min growth (not shown), the NWs exhibited similar morphologies as the ones obtained after 30 min. Consistent with our previous studies [15,19], the NWs grew predominantly perpendicular to the substrate surface, along the [1 1 1] B direction. For the longer growths (30 and 40 min), a minority of NWs grew at tilted angles, but no preferential orientation could be established. It is also evident that the conditions selected for the longer growth durations favored a strong tapering, which was isolated near the NW tip. This is illustrated in the inset of Fig. 1c, and is most noticeable for the NWs that were seeded from Au particles smaller than 50 nm in diameter. The dependence of tapering on Au particle diameter is further emphasized by the inset of Fig. 1b for the 10-min growth sample, where two types of structures, rod and taper-shaped NWs, could clearly be identified. The tapering was quantified using a series of SEM images such as the ones in Fig. 1, by introducing a "tapering ratio", defined here as the ratio of the NW diameter at its base to that at its tip. Measurement of the wires was performed manually, directly on the tilted-view images, without any discrimination of morphology (i.e. tapered and non-tapered). These ratios are shown in Fig. 2 as a function of the Au seed particle diameter d, where each data point represents one NW. After only 3 min of growth some tapering can already be observed. As previously discussed [15], and further emphasized in Fig. 2, there is a strong relation between tapering and the size of the particle. In general, smaller seed particles mean stronger tapering, while larger ones yield more rod-like structures. The observed range of tapering ratio for a given seed particle size is attributed to the non-uniform particle distribution