Generic nano-imprint process for fabrication of nanowire arrays

Aurélie Pierret¹, Moïra Hocevar¹,², Silke L Diedenhofen³, Rienk E Algra¹,⁴,⁵, E Vlieg⁶, Eugene C Timmering¹, Marc A Verschuuren¹, George W G Immink¹,⁶, Marcel A Verheijen¹,⁶ and Erik P A M Bakkers¹

¹ Philips Research Laboratories Eindhoven, High Tech Campus 11, 5656 AE Eindhoven, The Netherlands
² Delft University of Technology, 2628 CJ Delft, The Netherlands
³ FOM Institute for Atomic and Molecular Physics c/o Philips Research Laboratories, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands
⁴ Materials Innovation Institute (M2i), 2628 CD Delft, The Netherlands
⁵ IMM, Solid State Chemistry, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands
⁶ MiPlaza Technology Laboratories, Philips Research Europe, High Tech Campus 29, 5656 AE Eindhoven, The Netherlands

E-mail: e.p.a.m.bakkers@tue.nl

Received 4 November 2009, in final form 17 December 2009
Published 8 January 2010
Online at stacks.iop.org/Nano/21/065305

Abstract

A generic process has been developed to grow nearly defect-free arrays of (heterostructured) InP and GaP nanowires. Soft nano-imprint lithography has been used to pattern gold particle arrays on full 2 inch substrates. After lift-off organic residues remain on the surface, which induce the growth of additional undesired nanowires. We show that cleaning of the samples before growth with piranha solution in combination with a thermal anneal at 550 °C for InP and 700 °C for GaP results in uniform nanowire arrays with 1% variation in nanowire length, and without undesired extra nanowires. Our chemical cleaning procedure is applicable to other lithographic techniques such as e-beam lithography, and therefore represents a generic process.

Supplementary data are available from stacks.iop.org/Nano/21/065305/mmedia

1. Introduction

Semiconductor nanowires (NWs) have been intensely studied because of their highly tunable optical and electrical properties. They have been employed as functional elements in light-emitting diodes (LEDs) [1, 2], transistors [3] and antireflection coatings [4]. The vapor–liquid–solid (VLS) bottom-up growth process [5] allows growing (radial) core/shell structures or (axial) quantum dot heterostructures [6]. A metal nanoparticle is used as catalyst for nanowire growth, and can be deposited via spin-coating from a colloidal solution, spraying an aerosol solution, or by deposition of a thin film, which will break up by heating the sample. However, the density and position of the nanowires are not controlled using these approaches. We have previously observed [7] that the nanowire growth rate sensitively depends on the density and the dimensions of the gold particles. Such a variation of the growth rate can result in non-uniform optical or electrical properties. It is likely that, for instance, the dispersion of the electron mobility in InAs/InP core–shell nanowires [8] is related to the large spread in shell thickness of these nanowires grown from randomly deposited colloidal gold particles. Besides the axial growth rate, most probably also the radial (shell) growth is affected by the catalyst density. Hence, in order to improve the nanowire uniformity, it is important to control the position and density of the catalyst particles on the substrate. Different approaches have already been reported, such as e-beam lithography [9–11], gold deposition through an anodic aluminum oxide template [12] and nanosphere lithography [13]. In general, these techniques do not allow for large-area structuring because of either high cost or lack of long range order. Alternatively, nano-imprint lithography [14]
has been reported to define nanowire positions. This technique enables patterning of large surface areas at relatively low cost. However, this process has not been fully optimized and extra undesired nanowires were obtained. It has been shown that nanowire growth can be nucleated by organic molecules [15] and the undesired nanowires probably originate from organic residues from the photoresist.

We have developed and optimized a wafer scale soft nano-imprint method, called substrate conformal imprint lithography (SCIL), to control the position of InP and GaP nanowires. In order to fabricate uniform, defect-free nanowire arrays we have systematically studied the effect on nanowire growth of chemical and thermal treatment of the substrate which contained gold catalyst particles. These treatments were focused on the removal of organic residues from the photoresist layer. The process has been further optimized by adjusting the gold layer thickness. Finally, the quality of the grown nanowire material has been evaluated by optical characterization on InAsP quantum dots in InP nanowires.

2. Experimental details

Our substrate conformal imprint lithography method makes use of a flexible patterned stamp made from poly-di-methyl-siloxane (PDMS) [16] which is molded from a silicon master pattern which contained arrays of holes and was fabricated using e-beam lithography. The composite stamp is molded from the master following the procedure described in [16, 17] which yields a two-layer soft PDMS stamp with protruding pillars. The developed nano-imprint and lift-off process has the following steps. A ∼100 nm thick layer of poly-methyl-methacrylate (PMMA) is applied by spin-coating on full 2 inch wafer area is patterned with an array of holes with a diameter of 53.2 µm and an aperture NA of 0.65. Next, a precise amount of a 10 nm thick remaining residual sol–gel layer is deposited by spin-coating over the PMMA layer [18]. Within two minutes after the spin-coating process the stamp is applied in the still liquid sol–gel resist. The features in the stamp are filled by capillary forces with the sol–gel resist. The sol–gel reacts to form a solid silica glass in about 20 min, where residual solvents and reaction products (alcohols and water) are absorbed in the PDMS rubber. Finally the stamp is carefully removed from the patterned silica layer by peeling. In this way the full 2" wafer area is patterned with an array of holes with a diameter of ∼100 nm. The ∼10 nm thick remaining residual sol–gel layer between the bottom of the features and the PMMA layer is removed by a CF3–based reactive ion etch (RIE). Then oxygen RIE is used to transfer the pattern of the sol–gel layer into the underlying PMMA layer. The oxygen etch stops as the III–V material is reached and a short over-etch is applied in order to remove any residual PMMA. A short etch in a 1% HF solution removes the formed Ga or In oxide, after which a thin (1–6 nm) gold layer is deposited onto the patterned sol–gel/PMMA pattern by perpendicular evaporation. The lift-off process is performed in acetic acid which dissolves the PMMA layer and releases the silica and gold metal which is suspended by PMMA. This leaves precisely placed gold dots of controlled diameter and thickness on the semiconductor material. In this work different stamps were used with 90 and 100 nm hole diameters on a corresponding pitch of 0.5 µm (tetragonal) and 1 µm (hexagonal).

The lift-off process leaves (organic) residues on the substrate besides the patterned metal particles. Various chemicals were tested to clean the substrate surface. We investigated the effect of fumic nitric acid (HNO3), piranha (H2SO4:H2O2:H2O, 5:1:1), King’s water (HCl:HNO3:H2O, 3:2:3) and (1%) fluoric acid (HF) and bromine–methanol (Br2:MeOH, 1:103 or 1:25 × 103) on the NWs growth quality. After exposure to these chemicals at room temperature the samples were left in streaming deionized cold water for about 5 min.

The nanowires were synthesized in an Aixtron 200 metal–organic vapor-phase epitaxy (MOVPE) reactor from tri-methyl-gallium (TMGa) or tri-methyl-indium (TMIn) for the group III elements and phosphine (PH3) for the group V elements. For growth of an InAsP heterostructure, arsine (AsH3) was added. A thermal anneal was applied before nanowire growth for 10 min at different temperatures under a PH3 flow. During the thermal anneal the gold droplets form a eutectic, Au–In or Au–Ga, depending on the substrate. The native oxide layer covering the samples and residual organic materials are removed at an annealing temperature exceeding 550 °C.

Scanning electron microscopy (SEM) images were obtained with a Philips XL 40 FEG system. NW lengths and diameters were measured in these images by investigating 30 nanowires per array. The samples were studied with a Tecnai 300 keV TEM in both bright-field as well as in high-angle annular dark-field (HAADF) mode. The chemical composition of the nanowires was studied using scanning TEM in combination with energy-dispersive x-ray analysis (EDX). Microphotoluminescence measurements on InAsP heterostructure nanowires transferred on SiO2 substrates were performed at 4.2 K. The nanowire quantum dots were excited with a 532 nm continuous wave laser focused onto a spot size of 0.6 µm using a microscope objective with a numerical aperture NA = 0.85.

3. Results and discussion

Figure 1(a) shows an SEM image of the surface after the lift-off process without further treatment. We can clearly see the high fidelity of the pattern transfer, as the Au particles are arranged in an ordered pattern. However, extra material is present around the Au islands. EDX measurements, carried out with the SEM, show that these contaminants are carbon-based residues from the PMMA layer. The nanowires are grown by MOVPE on (111)B-oriented InP and GaP substrates, on which the Au particle arrays were patterned using SCIL. The SEM image in figure 1(b) is taken after InP nanowire growth. Besides nanowires grown from the predefined catalyst particles in a regular pattern, a lot of undesired thin nanowires are obtained. These extra nanowires arise if no or improper pre-treatment was used after the lift-off. This shows that growth of these extra nanowires is initiated by the organic material
Samples exposed to a piranha solution at 20 \degree C nanowires. The samples have been annealed at 550 \degree C anneal before growth. The Au layer thickness was 6 nm in all nanowire growth quality. The Au layer thickness was 6 nm in all cases. The samples have been annealed at 550 \degree C for InP, but samples indicated by an * have been annealed at 550 \degree C. The percentage of defects (undesired, missing or misplaced nanowires) is determined from a large number (400–2000) of nanowires.

Table 1. Influence of different chemical treatments on the InP nanowire growth quality. The Au layer thickness was 6 nm in all cases. The samples have been annealed at 550 \degree C for InP just before growth. The percentage of defects (undesired, missing or misplaced nanowires) is determined from a large number (400–2000) of nanowires.

| Solution      | Treatment time | Undesired | Missing | Misplaced |
|---------------|----------------|-----------|---------|-----------|
| HNO₃          | 5 min          | 10%       | <1%     | <1%       |
| HNO₃ + HF     | 5 + 1 min      | 14%       | <1%     | 7%        |
| King’s water  | 5 s            | 95%       | <1%     | 13%       |
| Piranha       | 30 s           | 2.5%      | <1%     | <1%       |

Table 2. Influence of different chemical treatments on the GaP nanowire growth quality. The Au layer thickness was 6 nm in all cases. The samples have been annealed at 700 \degree C for GaP, but samples indicated by an * have been annealed at 550 \degree C. The percentage of defects (undesired, missing or misplaced nanowires) is determined from a large number (400–2000) of nanowires.

| Solution                  | Treatment time | Undesired | Missing | Misplaced |
|---------------------------|----------------|-----------|---------|-----------|
| 1000 Br₂/MeOH             | 2 s            | 100%      | 5%      | 65%       |
| Piranha                   | 5 min          | 104%      | <1%     | 13%       |
| Piranha                   | 3 min          | 300%      | <1%     | <1%       |
| Piranha                   | 1 min          | 535%      | <1%     | <1%       |
| Piranha                   | 1 min*         | 6%        | <1%     | <1%       |
| Piranha + HNO₃            | 1 + 5 min*     | 9%        | <1%     | 6%        |
| HNO₃ + piranha            | 5 + 1 min*     | 5%        | 27%     | 15%       |

* Annealing temperature at 700 \degree C.

Figure 1. InP nanowire arrays by soft nano-imprint lithography. (a) Pattern of Au dots after lift-off process, prior to the growth of nanowires. (b) Nanowire array without suitable cleaning step prior to growth resulting in extra ‘grass-like’ wire growth between the patterned arrays. (c) and (d) Nanowire array with a piranha cleaning step and 550 \degree C anneal before growth.

Table 2 observed in figure 1(a). An extra cleaning step is necessary to remove the organics prior to growth, but it should not change the III–V substrate surface chemistry [19], since nanowire growth rates sensitively depend on the surface diffusion of the precursor molecules [7, 10]. We have investigated the effect of the following wet chemical treatments on the quality of the nanowire growth: fuming nitric acid, an acidic etchant, oxidizes InP and GaP. Piranha is a mixture that contains a very strong oxidizer which can remove organic residues. King’s water is a combination of a powerful oxidizer and strong acid, and Br₂/methanol is an electrochemical etchant for InP and GaP. After exposure to one of these solutions or a combination of them the samples were left in streaming deionized cold water for about 5 min. The results are summarized for InP and GaP in tables 1 and 2, respectively.

InP samples treated with King’s water, HNO₃, and (HNO₃ + HF) show a large number of undesired nanowires around the intended nanowires. During the longer treatments with King’s water, the gold has been removed and only undesired nanowires were grown (see supplementary information figure S1 (available at stacks.iop.org/Nano/21/065305/mmedia)). Samples exposed to a piranha solution at 20 \degree C show a very low density of undesired nanowires, as shown in figures 1(c) and (d). (Almost) no undesired nanowires were obtained and all the nanowires grew at the predefined position. The overview SEM image in figures 1(d) shows that the InP nanowire dimensions are uniform across the sample and that just a few nanowires are missing. The obtained InP nanowires have an inter-spacing of 500 nm, as defined by the mold, and a length of 1761±19 nm, which is only a spread of 1.1\%. Furthermore the nanowires are tapered and have a top diameter of 95 ± 4 nm and base diameter of 171 ± 4 nm. It is important to note is that all InP samples presented in the table have been thermally annealed at 550 \degree C before growth. The effect of the annealing temperature will be discussed below.

GaP samples treated with Br₂/MeOH, (HNO₃ + piranha), (piranha + HNO₃) or Piranha for 5 min show not only extra nanowires (due to inherent added contamination with each processing step) but also misplaced and/or missing nanowires. We believe that these chemicals can oxidize and/or etch the Au/GaP interface, which can result in the removal of Au particles from the surface. We found that, similar to the results for InP wires, piranha treatment gives the best results (see supplementary information figure S1 (available at stacks.iop.org/Nano/21/065305/mmedia)), and the optimum treatment time for GaP wire growth is 1 min. At shorter times more undesired NWs arise, but at longer times NWs tend to kink and some of them are missing, which is probably due to an overetching of the surface. The best results were obtained in combination with the higher annealing temperature of 700 \degree C. We will now show that an extra thermal annealing step is necessary to optimize the growth.

We have studied the effect of annealing temperature on the nanowire growth. The annealing was done after piranha treatment, but prior to the growth. It is well known that a thermal anneal at high enough temperatures can remove In₂O₃ or Ga₂O₃ from the substrate surface [20]. To the best of our knowledge it is not known if the photoresist residues can be removed or react with the metal oxides by thermal treatment. In figure 2 the effect of annealing on the growth of InP nanowires is shown. Clearly, too low annealing temperatures, or no annealing at all, results in undesired extra wire growth and irregular growth of the patterned nanowires (see figures 2(a) and (b)). An
annealing temperature of at least 550 °C proves to be sufficient for defect-free InP wire growth (figure 2(c)). At higher temperatures nanowires with a thicker base are obtained (figure 2(d)). Probably the surface chemistry changes at these temperatures and promote the lateral growth at the base of the nanowires. Similar results were obtained for the growth of GaP nanowires (see supplementary figure S2, available at stacks.iop.org/Nano/21/065305/mmedia). Whereas at an annealing temperature of 550 °C still undesired GaP nanowires are obtained, at a temperature of 700 °C the defect density is very low (see also table 2). The GaP nanowires show slight tapering, but do not have a thick base as observed for the InP nanowires when annealed at this temperature (see supplementary information figure S2 (available at stacks.iop.org/Nano/21/065305/mmedia)). Growth without chemical cleaning but with an annealing step prior to growth resulted in many undesired nanowires. This shows that the combination of piranha treatment with a sufficiently high annealing temperature is essential for both InP and GaP wire growth. The different optimum annealing temperatures for InP and GaP shows that the removal process is substrate-dependent and suggests that the metal oxides play an important role in removing the organic residues.

To define the pattern in our process, we have used PMMA in direct contact with the substrate surface. The organic contaminants, from which the undesired nanowires grow, are probably a product from the PMMA layer. Our cleaning process effectively removes these residues and this cleaning process should also work successfully for other lithographic techniques, such as e-beam, in which the same photoresist is used. This shows that we have found a generic method to clean the substrate surface after lithography and to avoid the growth of undesired nanowires.

Now that we have managed to control the NW position on a clean substrate, the growth parameters can be studied. In several papers that report on nanowire position control, it has been shown that the gold dots can break up into several droplets [9, 21], which resulted in several nanowires being produced from one intended gold island. Detailed studies of this phenomenon have been published for the growth of carbon nanotubes, where arrays are fabricated with the same techniques [22, 23]. We have investigated this effect by systematically varying the thickness of the gold layer from 1 to 6 nm. Clearly for 1 and 2 nm (see figures 3(a) and (b)) the gold dots split into several droplets (probably during the anneal), catalyzing the growth of several NWs close to each other. The gold splitting can be explained by the concept of surface tension. For a small thickness, the ratio surface/volume (or diameter/thickness) ratio is large and the islands have a pancake-like shape. Due to the surface tension the gold dots split up to form spherical particles, which will decrease the liquid/air interface. At a thickness of 4 nm (figure 3(c)) still a few extra nanowires grow: however, at 6 nm (figure 3(d)) no splitting of the gold droplet is observed.

In order to test the quality of the nanowires grown in the arrays, we have synthesized InP/InAsP/InP heterostructured nanowires from the nano-imprinted Au islands. The optical properties of the InAsP section sensitively depend on the segment length and As/P ratio. We have applied different growth times and AsH 3 flows to fabricate segments with different lengths and compositions. In figure 4(a) a representative tilted-view SEM image is shown. The overall wire length is determined to be 5 μm. The base of the wire (up to 2 μm) is tapered, but the top part has a constant diameter. Such wire arrays are interesting for their photonic properties. We have used TEM HAADF and EDX measurements to determine the length and composition of the InAsP segments. The segment shown in figure 4(b) has a length of around 22 nm and has a In50As37P13 composition. The quality of these nanowire segments has been studied optically by measuring the photoluminescence at 5 K. The nanowires were transferred on a SiO2 substrate to measure their optical properties, as the pitch between InP nanowires is too small to optically characterize standing single nanowires. Figure 4(c) presents the power
dependence of a 10 nm long $\text{In}_{50}\text{As}_{37}\text{P}_{13}$ segment in the InP nanowire. In figure 4(d) is shown that the exciton (1.358 eV) emission at low excitation power (linear dependence) and a biexciton line (1.354 eV) evolves at higher powers (superlinear dependence). The linewidth (FWHM) is 2 meV for both peaks, which is higher than previous results obtained on InP/InAsP/InP nanowires [6]. In parallel with the biexciton line, a peak appears at 1.398 eV, corresponding to the PL emission of the InP nanowire segments. We show in the inset the exciton and biexciton intensities dependence with the power and slopes of 1 and 2 are obtained for the exciton and biexciton. These results show that these dots grown using a nano-imprint technique have a good optical quality and pave the way to large scale opto-nanoelectronic applications and photonic applications.

4. Conclusions

A generic process has been developed to grow arrays of (heterostructured) InP and GaP nanowires. Substrate conformal nano-imprint lithography has been successfully used to pattern gold particles on the substrate. We have shown that the preparation of the samples before growth with piranha solution in combination with a thermal anneal is a significant step to obtain perfect arrays. We are able to pattern complete 2 inch wafers with perfect nanowire arrays with excellent uniformity. This cleaning procedure is applicable to other lithography techniques such as e-beam lithography, and therefore it is a generic process.

Acknowledgments

This research was carried out under project no. MC3.05243 in the framework of the strategic research program of the Materials Innovation Institute (M2i) (www.M2i.nl), the former Netherlands Institute of Metals Research, the FP6 NODE (015783) project and the Ministry of Economic Affairs in the Netherlands (NanoNed). This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO) and is part of an industrial partnership program between Philips and FOM. The authors thank H de Barse for SEM imaging. Correspondence and requests for materials should be addressed to E P A M Bakkers.

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