Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 812-813

H-5-2

InP Nodes in GaP-based Free-standing Nanowires on Si(111)

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1. Introduction

Semiconductor nanowires grown by vapor-liquid-solid (VLS) method are promising as building blocks in optical and electrical devices [1-5]. Recently reported vertical GaP nanowires grown on Si substrates have a possibility to apply to opto-electronic integrated circuits [1, 2]. For the growth of nanowires, by combining different materials, it becomes possible to form heterostructures in the axial and radial direction, and many structures have been reported in various material systems. We have succeeded in forming three-dimensional structures by alternating wire growth and capping growth in the AlGaAs system, and also in forming GaAs/AlAs heterostructures on GaP nanowires on Si(111) substrates [3, 4].

VLS-grown III-V nanowires tend to grow in the [111]B direction, and they are straight with a length of several micrometers. If we can make nanowires with nodes that can bend, the application field will be extended further. Such bending nodes are possible to use heterostructures in nanowires [5]. Inserting thinned or soft materials between thick or hard ones is a basic fabrication concept for creating nodes. At bending nodes, there would be active points that would emit photons or electrons or that make contact with molecules for chemical reactions or that just move mechanically, which would lead to nano-machines. In addition, several bending nodes could be connected to form a large curvature, which would lead to various three-dimensional structures like arches or coils.

Here, we show that InP can form an egg-like structure in GaP nanowires and also that InP can be selectively grown on the GaAs parts of GaAs/GaP nanowires, which are very useful in making bending nodes in nanowires.

2. Experiments

The wire growth was carried out in a low-pressure (76 Torr) horizontal metalorganic vapor phase epitaxy (MOVPE) reactor [2-5]. Trimethylgallium (TMGa) and trimethylindium (TMIn) were the group III sources. Tertiarybuthlphosphine (TBP), phosphine (PH_3) and arsine (AsH_3) were the group V sources. The catalysts were used Au particles (20 nm) from Au colloids. First, GaP nanowires were grown on Si(111) substrates. A small amount of GaP was grown for 5 s at 550 ˚C by introducing TMGa of 4.8×10^{-6} μmol/min and TBP of 4.5×10^{-4} mol/min. Then, GaP wire growth was performed at 480 ˚C by introducing the same source gasses. In order to make nodes, InP growth was performed between the GaP wire growth at 480 or 550 ˚C by introducing TMIn of $2.4\text{-}4.8\times10^{-6}$ mol/min and TBP of 4.5×10^{-4} mol/min. And GaAs growth was performed between the GaP wire growth at 460˚C by introducing TMGa of 4.8×10^{-6} mol/min and AsH_3 of 2.0×10^{-4} mol/min. InP capping growth was performed at 550 ˚C by introducing TMIn of $0.6\text{-}2.4\times10^{-6}$ mol/min and TBP of 4.5×10^{-4} mol/min.

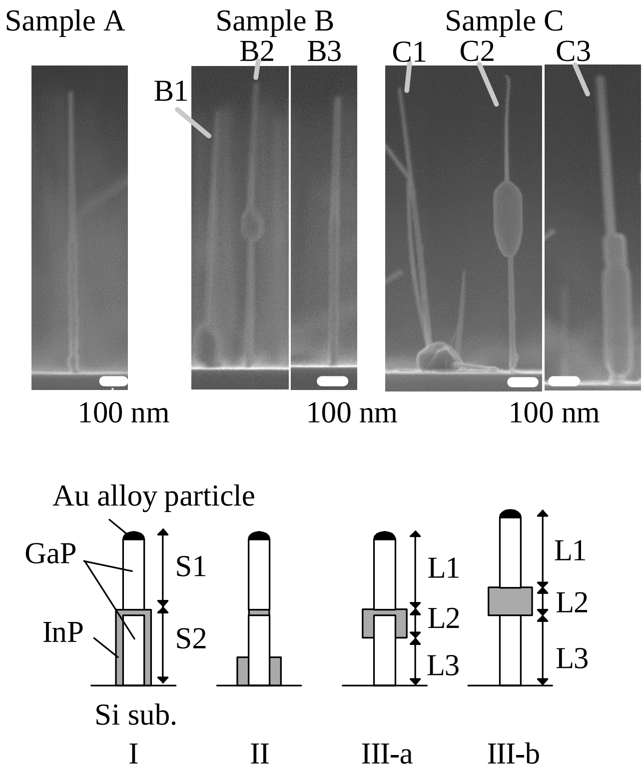

Fig. 1 Cross-sectional SEM images of GaP/InP/GaP nanowires. Sample A: InP at 480 ˚C for 20 s ([TMIn]= 2.4 μmol/min). Sample B: InP at 550 ˚C, others were the same for A. Sample C: InP at 550 ˚C for 1 min ([TMIn]= 4.8 μmol/min). And supposed schematic structures are shown below.

3. Results and discussion

Figure 1 shows SEM images of GaP/InP/GaP nanowires obtained with different growth conditions for InP. The first and last GaP wire parts were grown for one minute. For sample A, the growth temperature was the same for GaP and InP. For sample B and C, the growth temperature was higher for InP, but the TMIn flow rate was higher and the growth time longer for sample C. Three types of typical structures are schematically shown bellow the SEM images. For type I, the bottom GaP part is covered with InP, which is seen for all cases, i.e., samples A, B3, and C3.

In particular, most of the wires were type I for sample A. For type II, there is an InP block at the bottom of the wire, which can be seen for the high-temperature InP growth case of samples B1 and C1. And for type III, an InP block is formed at the middle of the wire, which can be seen in samples B2 and C2. The difference in the lattice constant between GaP and InP was large (7.7 %) so it seems difficult to cover entire GaP wire surface smoothly. The surface at the bottom region of sample A was very rough so the InP layer seems to be polycrystalline. At high temperature, adsorbed materials could have diffused on the GaP surface and formed an egg-like structure in the middle. But they could have also diffused to the bottom so that an InP block was also formed at the bottom as illustrated in type II. For type III, there are two possible structures (III-a and III-b). Since the growth times for the top and bottom GaP wire parts were the same, their lengths are almost the same, which could be evaluated in sample A, where the ratio of the bottom GaP to the top GaP (S2/S1 in type I) was 1.02 (=α). For the structures of B2 and C2, L3/L1=1.0 and 1.07, respectively. These values were close to α. And L2/L1=0.25 for B2 and 0.72 for C2, which make up a considerable part of each wire length and are much larger than the difference between L3/L1 and α. From these evaluations, the formed egg-like structures were thought to be type III-b.

We also confirmed room-temperature photoluminescence (PL) for the sample C (PL emission peak at 863 nm). InP nodes in the wires are good quality and very promising for photonic devices.

Next, we tried to form bending nodes using InP in GaAs/GaP-based nanowires. From the results for GaP/InP/GaP nanowires described above, it appears that the InP diffusion properties can be used for the selective growth. First, the base GaP wire part was grown for one minute at 480 ˚C. Then, a GaAs part was grown for 20 s at 460 ˚C. The growth of the GaP part at 480 ˚C and that of the GaAs part at 460 ˚C were alternated two times. Finally, after raising the temperature to 550 ˚C in the PH_3/H_2 gas, the InP capping growth was performed for 20 s.

As shown in Fig. 2, nanowires with two nodes were formed. From cross-sectional SEM images (not shown here), we determined the total length of the wire to be about 3190 nm, the first node to be about 1020 nm from the surface, and the second node to be about 2050 nm from the surface. From these values, we found that the GaAs was selectively capped with InP. The reason for the selective growth of InP on GaAs is thought to be that, compared with GaP, the lattice constant of GaAs is close to that of InP so that the InP could bond to the GaAs. In Fig. 2, bending can be seen at the top node. An explanation of the bending would be that the width of the GaAs part was selectively reduced as the temperature was raised for the InP growth. However, the bottom node does not show any apparent bend. Considering the tapered wire shape, a possible reason is that a thin GaP layer covered the GaAs, which prevented the width of the GaAs from reducing as the temperature was raised. At the top node, the GaP might be thin enough to allow the width of the GaAs to reduce. At the bottom node, GaAs was not so reduced and the width is thick enough to bear some external force.

How to make multiple bending nodes remains a big issue. Here, some spontaneously occurring force, perhaps a kind of electrostatic force, was exerted on our grown nanowires. To make controlled ordered bends, we need to apply some controlled force to the nanowires. We are now seeking a way to solve this issue.

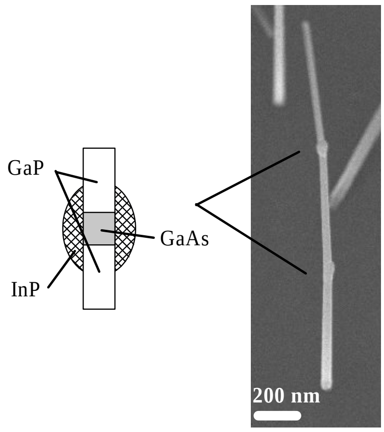

Fig. 2 SEM images of two InP-capped GaP nodes in GaP-based nanowires on Si (111), viewed 38˚ tilted from the normal direction.

4. Conclusions

We have investigated the formation of InP nodes in GaP-based nanowires as bending nodes. We showed GaP/InP/GaP nanowires where InP could form an egg-like structure at the middle. InP nanostructures of this sample had sufficient crystal quality to show room-temperature photoluminescence. We also succeeded in forming two InP-capped GaAs nodes in GaP-based nanowires on Si substrate. The bending node was formed at the top node in this nanowire. We plan to further investigate how to make multiple bending nodes in nanowires.

Acknowledgements

We thank Dr. H. Hibino, Dr. H Sanada and Dr. H. Gotoh for their fruitful discussions. We also thank Dr. H. Yamaguchi and Dr. Y. Tokura for their continuous encouragement throughout this work. This work was partly supported by JSPS KAKENHI (16206003, 18310074).

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