InP Nanowires on Graphene-Covered Micron Fe Wires

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Abstract
Freestanding InP nanowires were grown on graphene/Fe plates and graphene/micron Fe wires. A low decomposition rate of tertiarybutylphosphine (TBP) on graphene makes the growth of straight nanowires difficult.

1. Introduction
Recently, the large-scale growth of single-layer and few-layer graphene has been demonstrated by the roll-to-roll fabrication method, and the advanced technique of transferring graphene sheets to flexible plastic substrates has led to stretchable, foldable, and transparent electronics and optoelectronics [1]. Graphene layers can be formed on many kinds of flexible metals and can be fashioned into various structures easily by pressing, stretching, grinding, or cutting. With the direct growth of semiconductor on graphene-covered metals, the application field could be widely expanded by using various 3D structures as base substrates, and this would be a cost effective approach. So far, such direct growth on graphene/metal has not been investigated. Here, we report our preliminary attempts to grow nanowires directly on graphene/metal. The vapor-liquid-solid (VLS) mechanism is widely accepted as the base mechanism for freestanding nanowire growth from metal particles as catalysts. It is similar to the mechanism of liquid-phase epitaxy, but is driven catalytically in a nano-area by nanometer-scale metal particles, such as Au. This feature is very useful for fabricating nanodevices in electrical and optical circuits because of the feasibility of forming p-n junctions and various heterostructures like quantum dots and core-shell structures.

There are few reports concerning on the growth of semiconductor nanowires on graphite or graphene layers. Kim et al. reported vertical ZnO nanowires on a graphene region and randomly oriented ones on a SiO2 region [2]. Hong et al. reported the growth of InAs nanowires on patterned graphite surface [3]. We have recently reported GaP, GaAs, and InP nanowires grown on graphite and GaP nanowires grown on graphene/SiC by the VLS method using Au particles formed by Au deposition [4]. Further investigations are necessary for advancing the vertical nanowire growth technique on graphene.

2. Experiments
Substrates were polycrystalline Fe plates (99.995%) and micron Fe wires (99.5%) with a few graphene layers (two to three layers). Graphene was formed at high temperatures over 600 °C by supplying toluene gas in a simple vacuum chamber. The growth was carried out in a low-pressure metalorganic vapor phase epitaxy (MOVPE) reactor [4]. The carrier gas was palladium-diffused H2, and the flow rate was about 6.0 l/min. Trimethyl-indium (TMIn) was the group-III source, and TBP was the group-V source. Au particles were dispersed on the substrates by using Au colloids with a diameter of 10 nm. The growth was started by introducing TMIn and TBP simultaneously. We changed the growth time, V/III ratio, and growth temperature. After annealing at 550 °C, one-second InP growth was alternated five times followed by the InP nanowire growth at the growth temperature (Tg). The structures were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Energy dispersive X-ray spectrometry (EDS) analyses were also performed in the TEM chamber. To determine the elemental distribution in the nanowires, the Fe, P, In and C contents were evaluated from X-ray peaks in the EDS analysis.

3. Results and discussion
First, we investigated the InP-nanowire length versus growth time. For comparison, InP nanowires were also grown on Si(111) (without graphene layers) by using the same growth conditions. The nanowire length for graphene/Fe was two-thirds of that for Si samples at long growth times and showed gradual saturation. Both kinds of nanowires had similar tapered structures. On graphene, the nanowires were randomly aligned, which indicates that the crystal orientation was not uniquely determined at the initial stage in this growth condition, since the nanowire tended to grow in the [111]B (or [0001]B for wurtzite) direction. The tapered structure indicates that the growth temperature is relatively high, which results in enhancement of the vapor-solid growth at the side walls. We further investigated the V/III dependence of the grown structures. The V/III ratio was changed from 3200 to 1600 by reducing the TBP flow rate by half or doubling the TMIn flow rate. In both cases, ball-like structures formed on the surface. Such ball-like structures also formed as the temperature was decreased. On the other hand, when the temperature was increased, short nanostructures formed and there were no nanowires. The ball-like structures were also seen on graphene/SiC and HOPG at similar growth conditions,
and they were found to consist of only In from the EDS analysis. These results indicate that the decomposition rate of TBP is quite low on graphene. The HR-TEM images and EDS mapping images (Fig. 1) were taken at the boundary of an InP nanowire and graphene/Fe. Four- to five-layer graphene was clearly seen between the nanowire and the substrate in the HR-TEM image. The graphene is also seen in the C-mapping image in Fig. 1. Notably, the layer of FePₓ under the graphene layers can be seen in the P- and Fe- mapping images. During the growth, TBP decomposed and phosphorous was released on the surface. Phosphorous could diffuse into Fe even though the graphene covered the surface. There should be defects or openings at the domain boundaries in graphene through which phosphorous permeated. We have also tried to grow InP nanowires on graphene/Cu and graphene/Ni but were unsuccessful. For Cu and Ni, the reaction was so strong that it changed the surface morphology, which made the nanowire growth impossible. From the alloy phase diagram for Fe-C [5], Fe forms various alloy compounds with carbon, and by adding carbon, Fe becomes harder, which is known as steel. On the other hand, from the alloy phase diagrams for Cu-C and Ni-C [5], Cu and Ni are almost completely segregated from carbon so that their reactivity as metal remains. Thus the formation of steel would be important for the success of the subsequent InP nanowire growth. And by using a low growth temperature, the nanowire shape became straight. Despite the surface roughness of the Fe wire, many free-standing and straight nanowires grew outward like spines of cacti. This is a promising demonstration, which could lead to a new kind of fabrication method for some functional devices on micron wires.

The merit of using Fe metal is an easy process for 3D structures. And the covering graphene plays a role as the initial base surface for the growth of nanowires, which are unaffected by the polycrystalline Fe underneath the graphene. We have demonstrated InP nanowire growth on a micron Fe wire with a diameter of about 100 µm as shown in Fig. 2. First, graphene was formed on the wire. Then Au particles were dispersed using Au colloids. For the nanowire growth, after annealing at 550 °C, one-second InP growth was alternated five times followed by five-alternated one-minute InP growths at the growth temperature of 345 °C. At each interval, In atoms on the surface were reduced by evaporation so that the In could not aggregate enough to form ball structures.

4. Conclusions

We obtained freestanding InP nanowires on graphene/Fe plates and also on graphene/micron Fe wires. From the study of graphene/Fe-plate samples, we found that a low decomposition rate of TBP on graphene makes the growth of straight nanowires difficult. However, by inserting growth interruptions at a low growth temperature, straight nanowires could be formed on graphene/micron Fe wires, which is a promising result for future nanowire applications.

Acknowledgements

We thank Dr. H. Hibino and Dr. T. Sogawa for their fruitful discussions and continuous encouragement throughout this work. We also thank Drs. T. Mitate, T. Iizuka, and S. Mizuno of NTT Advanced Technology Corporation for their help in the TEM analysis. This work was partly supported by KAKENHI (23310097).

References