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Heteroepitaxy of Vertical InAs Nanowires on Thin Graphitic Films

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1. Introduction

Paradigm shift from rigid single-crystalline substrate to flexible ultrathin graphitic substrates has opened the great potentials for foldable, lightweight, and transparent electronics and optoelectronics [1,2]. Since the honeycomb carbon crystal lattice of graphene and graphitic layers can be well compatible with many semiconductors of zinc blende, and wurtzite crystal structures, the compound semiconductor fabricated on graphitic layer provides important hybrid junctions for the device applications. Nonetheless, problems associated with chemical stability of sp^2-bonded carbon atoms precluded the use as a substrate for heteroepitaxy. For the reasons, a few semiconductor or metal crystals have so far been deposited directly on graphitic surface [3,4]. Here, we present the critical leading factors of nucleation and growth for the heteroepitaxy of vertical inorganic nanowire arrays on honeycomb carbon surface by means of van der Waals (VDW) epitaxy. We fabricated vertical InAs nanowire arrays epitaxially on the graphitic substrates, and further achieved regular and uniform InAs nanowire arrays with designed procedures including surface etching and substrate patterning.

2. Results and discussion

The basic approach for fabricating InAs nanowires on graphitic surface is utilizing catalyst-free metal−organic vapour-phase epitaxy (MOVPE) and employing thin graphitic layers as a substrate that is mechanically cleaved from highly oriented pyrolytic graphite (HOPG). The thin graphitic films were transferred onto SiO_x-coated Si substrates, and were processed by oxygen reactive ion etching (O_2 RIE) to form atomic layer ledges or kinks on the graphitic surface. The InAs nanowires were grown directly on graphitic films with neither additional seed nor buffer layer.

Scanning electron microscopy (SEM) images of Figure 1(a)–(b) present the general morphologies of InAs nanowires grown on graphitic layers and patterned graphitic substrates. The low-magnification image shows that all the nanowires were grown perpendicular to the graphitic layers with a uniform diameter distribution (Fig. 1(a)). The vertically well-aligned InAs nanowires exhibited no tapering along the entire length of nanowires, as shown in Figure 1b, owing to the well-optimized MOVPE condition for unidirectional growth of InAs nanowires [5]. The SEM image of Figure 1(a) shows clearly, however, that not only nanowires but also islands were concurrently formed on the graphitic films. Figure 1(b) highlights that the InAs nanowires were selectively grown only on the hole-patterned graphitic layer: almost all hole patterns yielded InAs nanowires (~88 %), verifying high-yield growth process. Interestingly, the diameter of nanowires was not defined by patterned hole diameter, different from the selective-area growth of InAs nanowires on Si or III–V substrates. This hole-size-independent growth behavior can be elucidated by diameter-limited growth on the non-wetting graphitic surface.

In general, a significant driving force for heteroepitaxy is the minimization of substantial energy through a process where the dangling bonds of the substrate surface form the strong chemical bonds with the deposited materials. However, since the honeycomb carbon atoms in graphite and graphene layers have no dangling bonds, the epitaxy of InAs nanowire on graphitic layer is definitely distinguished from the conventional heteroepitaxy. This unconventional, non-covalent epitaxy is the VDW epitaxy, first demonstrated by Koma *et al* [6]. However, reports of VDW epitaxy have been confined to the two- or three-dimensional crystal growths: no VDW epitaxy of vertical one-dimensional nanostructures have so far been reported. We note that the heteroepitaxy of InAs nanowires on graphitic layers is classified into quasi-VDW epitaxy in accordance with the previous report.

The VDW epitaxy of vertical InAs nanowire arrays is strongly related to the in-plane lattice match between InAs and honeycomb carbon lattice of graphitic layers. The distance of the nearest neighbor carbon honeycombs along <110> is 4.26 Å, which corresponds to thrice the distance of the nearest carbon atoms (= 1.42 Å) in the graphene layer. This value has a small misfit of only 0.47 % with the nearest arsenic–arsenic distance of 4.28 Å in InAs. Accordingly, it is energetically favorable when the primitive lattices of InAs fix up their positions upon the hollows of each carbon honeycomb along the lattice-matched <110> of *c*-plane graphitic surface. This substantial energy saving contributes to the heteroepitaxy of InAs(111)[110] ∥ graphite(001)[110], as confirmed by transmission electron microscopy and diffraction patterns shown in Fig. 1(e). Meanwhile, vertical InAs nanowires grow along [111]B orientation, hence the bottom layer of nanowire consists of (111)A. The adatom layer in the InAs (111)A basal plane, weakly bound to the graphitic surface, undergoes reconstruction at the initial growth stage. In accordance with the previous theoretical and empirical report on InAs (111)A surface [7,8], it is reasonably expected that the initial InAs

(111)A basal layer forms extremely flat honeycomb lattice surface with an indium vacancy in each InAs (111)A–2×2 unit. Because the indium and arsenic adatoms are at the same height level, this reconstructed flat InAs (111)A bottom layer with a small misfit of 0.47 % maximize the VDW bonding forces which enables the formation of vertical nanowire morphology with strong enough cohesive energy, even though the VDW bond energy is much smaller than the covalent bond energy (typically a few eV) by two or three orders of magnitude.

We have further explored the VDW heteroepitaxy for vertical GaAs nanowire arrays on honeycomb carbon surface, but the non-wetting graphitic surface only yielded GaAs island morphologies mostly along the step-edges of graphitic layers (Fig 1(c)) even under well-optimized epitaxial nanowire growth condition [9]. The neighboring GaAs islands did not show the in-plane alignment, implying non-epitaxial growth of GaAs on graphite. Since the VDW force is basically the universal force between molecules or atoms, GaAs can be easily deposited on the graphitic layer even without the epitaxial relationship. Previous theoretical calculations for metal adatom adsorption on graphene describe that energetic and structural properties of gallium and indium adatoms on graphene are analogous to each other in the same approximation condition. Accordingly, the lack of epitaxial relationship can be attributed to the large lattice mismatch of –6.22 % between the As–As distance in GaAs and the honeycomb–honeycomb distance along <110> in graphite. This observation supports the argument that the lattice coherent matching is very crucial in the VDW heteroepitaxy for vertical nanowire formation.

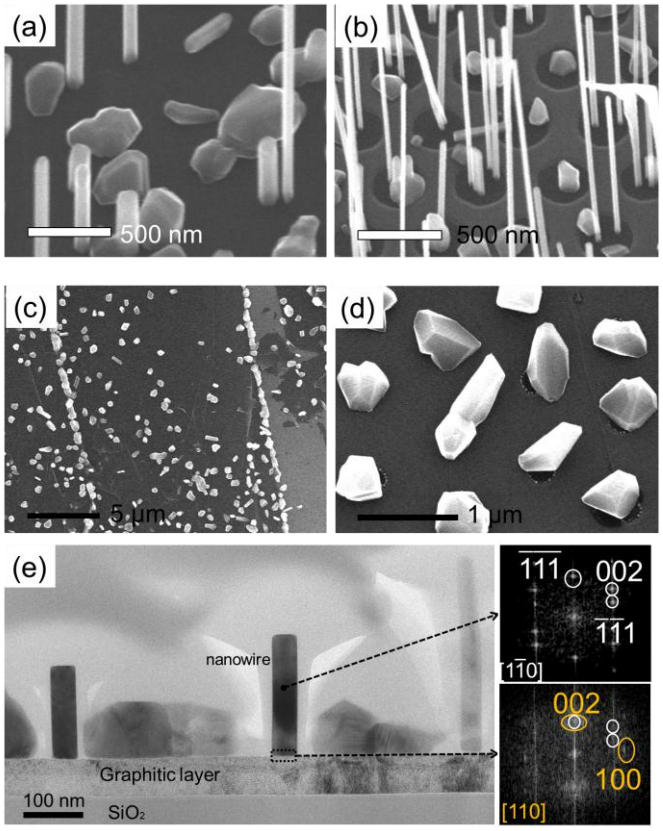

Fig. 1 SEM images of InAs nanowires grown on (a) graphitic films and (b) patterned graphitic layers. GaAs nanostructures were grown on (c) graphitic layers and (d) patterned graphitic layers, under the well-optimized GaAs nanowire growth condition. (e) TEM image of InAs nanowires grown on graphitic films. Insets are the diffraction patterns obtained from the area of InAs nanowire (upper panel) and the interface of InAs nanowire/graphitic film (bottom panel), showing the heteroepitaxial relationship.

3. Conclusions

We have demonstrated the critical leading factors for the epitaxy of inorganic vertical nanowire on graphitic materials. The in-plane lattice coherency and controlled surface ledge contributed to the epitaxial formation of vertical InAs nanowire arrays. The VDW heteroepitaxy, composed of InAs nanostructures grown directly on graphitic surfaces, opens a new understanding for preparing epitaxial heterojunctions utilizing honeycomb carbon materials.

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