Crystal phase and growth orientation dependence of GaAs nanowires on Ni_xGa_y seeds via vapor-solid-solid mechanism

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One of the challenges to utilize high performance III-V compound semiconductor nanowires (NWs) for large-scale technological applications is to control the crystal phase and growth orientation for homogenous nanowire properties. Here, we report the dependence of crystal structure and growth orientation of GaAs NWs on Ni_xGa_y seeds via vapor-solid-solid mechanism. The crystal structure of catalytic seeds is found to direct the crystal phase of NWs with cubic NiGa seeds yielding zincblende GaAs NWs while hexagonal Ni_2Ga_3 seeds producing wurtzite GaAs NWs. Furthermore, the seed/nanowire interface plane relationship would dictate the epitaxial growth orientation of NWs, which is independent of the NW diameters and growth conditions. All these suggest the importance of well-controlled phase and orientation of catalysts for the synthesis of homogenous nanowires. © *2011 American Institute of Physics*. [doi:10.1063/1.3630006]

In recent years, III-V compound semiconductor nanowires (NWs) such as indium arsenide (InAs) and gallium arsenide (GaAs) have attracted extensive research attention in electronics, photonics, and solar cells, due to their superior carrier mobilities and unique coupling effect with light.[1–6] However, the fundamental properties of NWs are highly dependent on their crystal phases and growth orientations; for example, the wurtzite (WZ) domains in zincblende (ZB) InAs NWs would act as electron scattering centers which significantly degrade the electron mobility of NWs.[7] In this regard, controlling crystal phases and growth orientations of NWs during the synthesis is extremely important in order to utilize them for technological applications.

In typical chemical vapor deposition (CVD) and molecular beam epitaxy approaches, NWs are always grown along different crystallographic directions with mixed crystal phases via the vapor-liquid-solid and/or vapor-solid-solid (VSS) mechanisms.[8–12] These growth instabilities are usually attributed to the diameter- or strain-induced fluctuation in surface free energies for different NW growth directions with different orientations in the sidewalls.[10,11] It is also noted that the catalytic seeds play a key role in the NW growth,[1,9] but it has not been well-addressed how the seeds affect and control the crystal phases and growth orientations of NWs during the growth, which are essential to achieve the synthesis of homogeneous high-perfromance NWs for large scale applications.

Recently, utilizing Ni as catalytic seeds, we developed a simple growth technique to synthesize crystalline, stoichiometric, and dense GaAs NWs on amorphous SiO_2 substrates via VSS mechanism.[12] In this letter, we emphasize on the dependence of crystal phase and growth orientation of GaAs NWs on Ni_xGa_y catalytic seeds. The crystal structure of seeds is found to direct the crystal phase of NWs with cubic NiGa seeds yielding ZB GaAs NWs and hexagonal Ni_2Ga_3 seeds producing WZ GaAs NWs. Also, the interface between the seed and NW would dictate the growth orientation of NWs, which is independent of the diameters of NWs and process conditions.

During the growth, GaAs powders were heated at 900 °C to produce Ga and As_2 precursors from the upstream zone of a two-zone furnace and the annealed Ni thin film catalyst (0.5 nm on 50 nm SiO_2/Si) was heated at 600 °C in the downstream zone. The carrier gas was 100 sccm H_2 (99.9995%) and the pressure was set at 0.5 Torr. After 30 min of growth, the system was cooled down to room temperature to collect the GaAs NWs. The NWs were then suspended in the anhydrous ethanol with ultra-sonication and drop-casted onto the copper grid for the high resolution transmission electron microscopy (HRTEM) and energy dispersive x-ray spectroscopy (EDS) with the microscope JEOL 2100F.

In this work, more than 40 individual GaAs NWs are studied. There is over 90% of NWs grown with cubic NiGa seeds (lattice constant, a = 0.289 nm) while the rest are grown with hexagonal Ni_2Ga_3 seeds (lattice constants, a = 0.405 nm and c = 0.489 nm). As shown in Figure 1, cubic NiGa seeds with different orientations are all appeared in the rectangular-like shape with NWs growing in the cubic ZB structure along both the ⟨111⟩ and ⟨110⟩ directions as determined by the plane spacing in the HRTEM imaging and corresponding reciprocal lattice spots extracted by fast fourier transform (FFT) (data not shown). Among those, majority of NWs studied (>90%) have the seed/NW interface orientation relationship of NiGa{110}|GaAs{111} (Figure 1(a), ∼50%) and NiGa{111}|GaAs{111} (Figure 1(b), ∼40%) while the rest have the relationship of NiGa{210}|GaAs{110} (Figure 1(c)). Notably, the NWs are preferentially grown along the ⟨111⟩ direction as this growth direction involves the lowest free energy crystal planes and thus more thermodynamically favorable;[13] however, NWs are also found to grow along ⟨110⟩ direction with the similar

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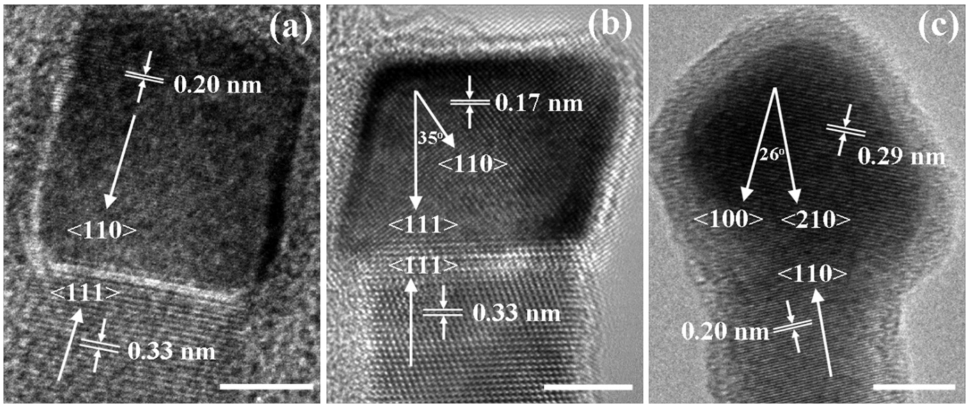

FIG. 1. HRTEM images of ZB GaAs NWs with different catalytic seed/NW interface plane orientations: (a) GaAs{111} NW catalyzed by the cubic NiGa{110} seed; (b) GaAs{111} NW directed by the cubic NiGa{111} seed; and (c) GaAs{110} NW grown with the cubic NiGa{210} seed. (Scale bars = 5 nm.)

NW diameters (Figure 1(c)). All these suggest that there are two separate growth mechanisms to synthesize GaAs NWs with different orientations independent of NW diameters and process conditions, which is different from the observations of diameter-controlled NW orientation in Si NWs and others.[14,15]

At the same time, as shown in Figure 2, a small amount of GaAs NWs (∼10%) are grown in the hexagonal WZ structure along the $\{10\bar{1}0\}$ direction with hexagonal Ni_2Ga_3 catalytic seeds appeared in the pentagonal-like shapes. The hexagonal structures of the seed and NW are confirmed by both the plane spacing in the HRTEM imaging and corresponding reciprocal lattice spots extracted by FFT (Figures 2(b) and 2(c)) while the seed/NW interface orientation relationship is determined to be $Ni_2Ga_3\{10\bar{1}0\}|GaAs\{10\bar{1}0\}$. Together with the cubic case observed in Figure 1, the crystal structure and growth direction of NWs are highly dependent on the phase and orientation of catalytic seeds. Notably, all studied seeds have no detectable As content and exist in non-spherical shapes which again confirm the VSS growth mechanism.[12,16] Specifically, since both NiGa and Ni_2Ga_3 alloys have relatively high melting points of ∼1200 °C (Ref. 17) which are much higher than the growth temperature of 600 °C, the catalytic seeds are believed to exist in the solid-state during the growth, instead of the molten form. As a result, it is plausible to deduce a VSS growth mode or a more general preferential interface nucleation (PIN) mechanism[18] in the GaAs NW growth.

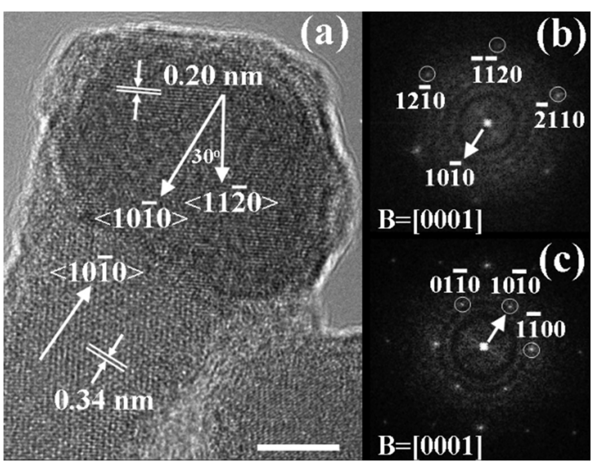

FIG. 2. (a) HRTEM image of WZ $GaAs\{10\bar{1}0\}$ NW directed by hexagonal $Ni_2Ga_3\{10\bar{1}0\}$ catalytic seed (scale bar = 5 nm), and (b) and (c) are the corresponding FFT of the catalytic seed and the NW body lattices, respectively.

According to VSS or PIN growth mode, Ga constituents are supersaturated from the catalyst and react with As_2 at the seed/NW interface;[18] therefore, similar to the epitaxial growth of semiconductor thin films on substrates,[19] the orientation relationship at the interface would direct the structure and growth direction of resultant NWs grown from the seed. In this regard, since ZB GaAs has a lattice constant of a = 0.565 nm which is close to two times of the one in cubic NiGa seeds (0.289 × 2 = 0.578 nm),[20] ZB GaAs NWs would prefer to grow epitaxially from cubic seeds. On the other hand, WZ GaAs has the lattice constants of a = 0.391 nm and c = 0.644 nm which are significantly different from those of the hexagonal Ni_2Ga_3 seed, so that WZ GaAs NWs are thermodynamically unfavorable to be grown; as a result, less than 10% of NWs are observed with WZ structure in this study. Similarly, other Ni_xGa_y alloys such as Ni_3Ga (cubic phase, a = 0.359 nm) and Ni_3Ga_5 (orthorhombic phase) cannot lead to any favorable GaAs NW growth due to the relatively large lattice mismatch or symmetry difference. Therefore, the crystal phase of GaAs NWs is determined by the corresponding catalyzing Ni_xGa_y seeds during the growth.

Apart from the crystal structure, the growth orientation of NWs is also dictated by the interface orientation relationship. Figure 3 shows the schematics demonstrating the interface plane relationships with the possible in-plane configuration of NWs studied in Figure 1. As depicted in Figure 3(a), the seed/NW interface has the interface plane relationship of NiGa{110}|GaAs{111} with the in-plane lattice mismatch of −2% ($NiGa\langle 1\bar{1}0\rangle$//$GaAs\langle 1\bar{1}0\rangle$) and 16.5% ($NiGa\langle 001\rangle$//$GaAs\langle 11\bar{2}\rangle$), where the lattice mismatch is defined as $[(a_{GaAs} - a_{NiGa})/a_{GaAs}]$. Figure 3(b) depicts the interface plane relationship of NiGa{111}|GaAs{111} with the in-plane lattice mismatch of −2% ($NiGa\langle 1\bar{1}0\rangle$//$GaAs\langle 1\bar{1}0\rangle$) and −2% ($NiGa\langle 11\bar{2}\rangle$//$GaAs\langle 11\bar{2}\rangle$). These two orientations are the most favorable in the aspect of minimal lattice mismatch among all other low-index interface relationships in the cubic system as compiled in Table I. On the other hand, there is another favorable NW growth orientation of NiGa{210}|GaAs{100} as the lattice mismatch is relatively minimal; however, GaAs{100} phase has a much higher free energy compared to the GaAs{110} and GaAs{111} (Ref. 13) so that this configuration is not thermodynamically favorable and indeed not being observed in this study.

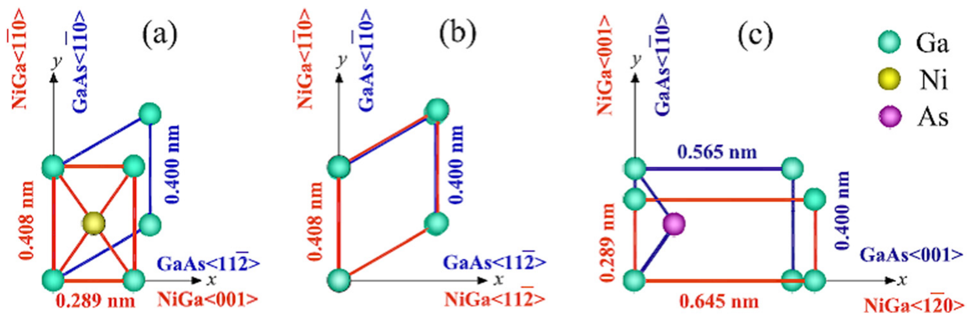

FIG. 3. (Color online) Schematic view of the in-plane orientation of the catalytic seed/NW interface: (a) NiGa{110}|GaAs{111}, (b) NiGa{111}|GaAs{111}, and (c) NiGa{210}|GaAs{110}.

Furthermore, catalytic seeds, with the NiGa{110} phase, consist of non-polar stacking plane where both Ni and Ga atoms existed in the seed/NW interface plane (Figure 3(a)). Even though atomic diffusion is known to be isotropic in metallic alloys, existence of these Ga constituents in the interface in Figure 3(a) is believed to facilitate the reaction with As_2 for the formation of NWs. This is in distinct different to the polar plane configuration in the NiGa{111} phase (Figure 3(b)) in which Ga atoms are required to diffuse through a barrier of Ni atomic plane for the NW formation. In this regard, the interface plane orientation of NiGa{110}|GaAs{111} is presumed to be more preferable than NiGa{111}|GaAs{111} which is in good agreement with our experimental results that majority of NWs studied have adapted this configuration. Besides, no WZ GaAs{0001} NWs are observed even though they have a small lattice mismatch (−3%) with the hexagonal Ni_2Ga_3{0001} seed, which can also be attributed to the inefficient Ga diffusion in the Ni_2Ga_3⟨0001⟩ polar direction due to the anisotropic diffusion in hexagonal crystal phase.[21]

Our results also call into question whether controlling the crystal phase and growth orientation of NWs can be purely accomplished by just tuning the NW diameters and growth conditions. Furthermore, the reported results show that special care needs to be taken preparing catalysts for the NW growth. For example, in this study, catalytic seeds with different crystal orientations would yield NWs with various phases and growth orientations as shown in Figures 1 and 2. This suggests the importance of a good control of seeds for homogeneous NWs for technological applications.

TABLE I. ZB GaAs NWs growth direction dependence on the NiGa alloy seed considering the seed/NW interface lattice mismatch.

Lattice mismatch (%)	NiGa (100)	(110)	(111)	(210)
ZB GaAs				
(100)				
x-direction	−2	−2	−24.7	−2
y-direction	48.8	27.8	27.8	−14.2
(110)				
x-direction	27.8	27.8	11.8	27.8
y-direction	48.8	37.8	37.8	−14.2
(111)				
x-direction	16.5	16.5	−2	16.5
y-direction	27.8	−2	−2	−61.3

In conclusion, GaAs NWs are grown epitaxially from Ni_xGa_y catalyst seeds via VSS growth mechanism. The crystal phase and growth orientation of GaAs NWs are highly dependent on corresponding seeds, which is attributed to the seed/NW interface in-plane lattice mismatch and effectiveness of Ga diffusion through the interface. This epitaxial growth holds a great promise to the development of homogeneous GaAs NWs preparation by controlling the Ni_xGa_y catalyst composition and orientation.

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