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Self-regulating and diameter-selective growth of GaN nanowires

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Abstract

We report diameter-selective growth of GaN nanowires (NWs) by using mono-dispersed Au nanoparticles (NPs) on a ligand-modified Si substrate. The thiol-terminal silane was found to be effective in producing well-dispersed Au NPs in low density on Si substrates so that the agglomeration of Au NPs during growth could be avoided. The resultant GaN NWs exhibited a narrow diameter distribution and their mean diameter was always larger than, while keeping a deterministic relation with, the size of the Au NPs from which they were grown. A self-regulating steady growth model is proposed to account for the size-control process.

1. Introduction

Recently, semiconductor NWs [1, 2] have attracted considerable attention as building blocks in electronics [3], optoelectronics [4], and sensors for specific molecular detection [5]. They are of fundamental importance for their special quantum behaviour in band gap engineering [6] and transport mechanisms [7]. Among various semiconductor materials, GaN having a wide direct bandgap is a highly promising material in optoelectronic and electronic applications, such as light-emitting p–n junctions and lasers, as well as logic circuits [8–11]. It has already been realized that further exploration and exploitation of new physics and novel devices associated with the NWs will require reliable control of size-selectivity processes.

Previously, we reported the preparation of high-quality GaN NWs by the chemical vapour deposition (CVD) method using gallium and ammonia as precursors [12]. It is known that metal NPs can be used to both catalyze the growth and control the size of the NWs through the vapour–liquid–solid (VLS) mechanism. However, the synthesis of NWs with a narrow diameter distribution with a mean value in the strong-confinement regime is still quite challenging.

The Au NPs, reported to be effective for growing the NWs of InP [13], Si [14], and GaAs [15], were found to be catalytically inactive for GaN due to the poor solubility of N in Au [16]. Therefore, the 3rd row transition metals, such as Fe and Ni, have been most commonly used as catalysts in the VLS growth of GaN NWs, because of the better solubility of Ga and N in the liquid metals [12, 16–18]. However, the main drawback of using Fe and Ni catalysts is the generation of contamination in the GaN NWs and the corresponding unwanted variation in their electronic properties. A recent computational study [19] observes low defect formation energy for Ni substitution (1.2 eV) in GaN, where Au substitution gives higher defect formation energy (~4 eV). One can expect, thus, much less diffusion of Au atoms into the lattice of GaN. This renders Au a better choice of catalyst for synthesizing GaN NWs from the point of view of product purity. Other advantages of using Au NP are the simplicity in better size-control and the synthesis of NPs having a size below 10 nm. The detailed preparation method for sized-controlled Au NPs can be found elsewhere [20, 21].

In this paper, we present the result of the size-control of GaN NWs using mono-dispersed Au NPs on Si substrate with a ligand modifier, which was used to increase the affinity between Au and Si while avoiding the aggregation of

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Figure 1. The SEM images of Au NPs on (a) thiol-terminated (MPTMS) Si substrate and (b) amine-terminated (APTMS) Si substrate. 12 nm Au NPs were used in both cases to clarify the difference in the number density of Au NPs. The white scale bars correspond to 100 nm.

Au NPs during the CVD process. High-resolution transmission electron microscopy (HRTEM) was employed to investigate the structure of the GaN NW and its interface with the Au NP. Systematic studies of the relationship between the size of the Au NPs, produced by the citrate reduction method, and the diameter of the resultant GaN NWs were performed and an empirical relationship was established over a range of sizes. Finally, as an attempt to address the size-selective phenomena, a self-regulating growth model is proposed.

2. Experimental details

Si wafers, used as the substrate for the growth of GaN NWs, were first rinsed in a buffered HF solution and then immersed in SCI solution for further cleansing and enhancing the surface Si–OH coverage to be ready for surface functionalization. The Si surface was modified by thiol-terminal 3-mercaptopropyltrimethoxysilane (MPTMS) or amine-terminal 2-aminopropyltrimethoxysilane (APTMS). The modified Si substrate thus possesses higher affinity toward Au NPs due to the strong binding interaction between gold and the ligand. Modified substrates were then immersed in the Au NP solution, which were prepared by the citrate reduction method [22]. More specifically, we chose the citrate reduction of HAuCl_4 in water. The ratio between the reducing/stabilizing agents and Au(III) (the tri-sodium citrate-to-gold ratio) was varied to control the size of Au NPs from 3 nm to 100 nm. Four Au NP samples of different average diameters (3.2 ± 0.8 nm,

Figure 2. XPS result of MPTMS-modified Si substrates after being immersed in Au NP solution.

(This figure is in colour only in the electronic version)

7.2 ± 1.0 nm, 12.0 ± 2.0 nm, and 20.4 ± 3.4 nm) were prepared and examined using the UV–visible spectrum and HR-TEM.

Finally, GaN NWs were grown on the mono-dispersed Au NP-deposited substrates by using molten gallium as a source material and NH_3 as a reactant gas in a quartz tube furnace. The quartz tube was de-gassed under vacuum and purged with NH_3 . The temperature of the furnace was increased to 920°C from room temperature at a rate of $50^\circ\text{C min}^{-1}$ and kept at 920°C for 3 h under a constant flow (10 sccm) of NH_3 . At this temperature, the organic groups on the Au surface were destroyed and catalytic growth of GaN could then proceed on the bare surface of gold NPs. After the furnace was cooled to room temperature, white-blue material was found on the surface of the substrate.

X-ray photoelectron microscopy (XPS, VG Scientific, ESCALAB 250) was performed to characterize the surface condition before the growth of NWs. The morphologies and crystal structures of the resulting materials were characterized using field-emission scanning electron microscopy (FESEM, JEOL, JSM-6700F) and x-ray powder diffraction (XRD, Toshiba, A-40-Cu). Further structural and elemental analyses on single NW were performed using high-resolution transmission electron microscopy (HR-TEM, JEOL-400 EX at 400 kV), selected-area electron diffraction (SAED), and energy-dispersive x-ray spectroscopy (EDX).

3. Results and discussion

Comparing the surface of the untreated and different ligand-modified Si substrates after immersion in the Au NP solution, we found that the MPTMS-modified substrate has a lower density of Au NPs and less aggregation of Au NPs compared with the unmodified substrate or APTMS-modified substrate. On the MPTMS-modified surface, the Au NPs have been observed to maintain their individuality (figure 1). The lower density could be due to the repulsive force resulting from the partial charges on the Au particles. We have also measured the XPS spectrum for the MPTMS-supported Au NPs. The presence of the two main peaks (figure 2) at 83.5 eV and 87.1 eV represents the doublet for $\text{Au}^0 4f_{7/2}$ and $4f_{5/2}$ [23]. The energy shifts of sub-bands at 84.9 eV and 88.5 eV are

Figure 3. (a) Low-magnification SEM image of GaN NWs on the substrate after the growth process. (b) High-resolution SEM images of GaN NWs grown by using 3.2 ± 0.8 nm Au NPs as catalysts. (b) Inset: back-scattered electron image of a GaN nanowire.

consistent with that reported by McNeillie *et al* and can be ascribed to the Au^I in an Au–octanethiol complex [24]. Thus, Au NPs were indeed attached to the substrate by the formation of chemical bonding with the sulfur atoms at the end of the modified group. On the other hand, the Au NPs on APTMS are much denser and have been aggregated. At high temperature during the CVD process, the Au NPs would further sinter to an even bigger size. Since a lower number density and lesser aggregation of Au NPs on the substrate are desirable for better controllability of the size-selective growth of GaN NWs, thus, hereafter, we only report the results using MPTMS as the anchoring agent for growth substrate modification.

After the GaN growth process, a thin layer white-blue in colour was observed on the surface of the substrate. A low-magnification SEM image (figure 3(a)) reveals uniform coverage of our resulting materials. High-magnification SEM images of GaN NWs (figure 3(b)) show that GaN NWs are straight in morphology and $\sim 2\text{--}7\ \mu\text{m}$ in length. A catalytic bead with higher atomic contrast can be observed at the end of the NW from the back-scattered electron image (figure 3(b), inset). High-intensity precision x-ray diffraction analysis of these samples (spectra has not given here) revealed a hexagonal wurtzite structure with lattice constants of $a = 3.182\ \text{\AA}$ and $c = 5.178\ \text{\AA}$. The HR-TEM image (figure 4) further reveals the structural details of the GaN NWs. The SAED pattern (figure 4, inset) can be indexed to the hexagonal GaN crystal along the [001] direction. The corresponding lattice-resolved image (figure 4) shows a single-crystalline structure of the individual NW. The spacing of ~ 0.272 nm between

Figure 4. Typical HR-TEM image and its corresponding SAED of a GaN NW. The direction of the long axis is parallel to the [100], and the zone axis is [001]. The diameter of this NW is ~ 13 nm. The spacing of 0.272 nm between arrowheads corresponds to the distance between two (100) planes.

Figure 5. HR-TEM images of two GaN NWs having diameters of (a) 15.8 nm and (b) 16.8 nm; the dashed circles represent the corresponding catalyst seeds with diameters of (a) 6.8 and (b) 7.1 nm.

the arrowheads corresponds to the distance between two (100) planes, which is in good agreement with that derived from the XRD and SAED results. In our TEM analysis, the growth direction of GaN NWs is always parallel to the (100) planes and no other growth direction is found. It indicates that the GaN NWs are much more phase-pure than our previous results using other transition metals as catalysts [12].

Figure 5 (typical TEM images of the tip of two NWs) reveals that the diameters of two wires are 15.8 nm and 16.8 nm and those of the corresponding catalyst seeds (figure 5, the dashed circles) are around 6.8 nm and 7.1 nm, respectively. Note that the size of the catalyst at the tip of the NW is similar to that before the growth process. A careful study of a sample of a number of NWs has confirmed that the size of the Au catalysts (NPs) at the tips of the NWs remained within the size-range of the starting Au NPs. It suggests that there was a little coagulation of the Au NPs during the CVD process. Statistical analyses of TEM micrographs further reveals that the diameter of the GaN NW depends on the Au NP size and the diameter distribution of the NWs being considerably narrower compared with those reported in the literature [25, 26]. A representative diameter distribution for the GaN NWs grown from Au NPs of 7.2 ± 1.0 nm is shown in figure 6. By using Au NPs of controlled diameters at 3.2 ± 0.8 , 7.2 ± 1.0 , 12 ± 2.0 , and

Figure 6. Representative diameter distribution for the GaN NWs of 16 ± 3.0 nm (black bars) grown from Au NPs of 7.2 ± 1.0 nm (hatched bars). The result of the diameter distribution was estimated from TEM images.

Table 1. Statistical table. (This table shows the mean diameter of the starting Au NPs and the corresponding GaN NWs for four sets of samples. (Mean value $\pm$ standard deviation).)

Au NPs (nm)	GaN NWs (nm)
3.2 ± 0.8	10.8 ± 2.3
7.2 ± 1.0	16.0 ± 3.0
12.0 ± 2.0	27.2 ± 3.8
20.4 ± 3.4	51.1 ± 7.1

20.4 ± 3.4 nm, the mean diameters of the corresponding GaN NWs were found to be 10.8 ± 2.3 , 16.0 ± 3.0 , 27.2 ± 3.8 , and 51.1 ± 7.1 nm, respectively (table 1). A linear relationship with a slope of 2.4 has been observed, indicating a stable growth condition in our experiment. The range of the size of GaN NWs is comparable to those reported recently using Ni thin film [18]. Moreover, in our method, we have a continuous range of mono-dispersed sizes of Au NPs to select. The fact that a clear positive correlation was observed between the size of the catalytic Au NPs and the diameter of the grown NWs also confirms that our process is promising for size-selective growth.

Although Au is not considered to be a good candidate, the successful growth of Au catalyzed GaN NWs has been achieved by several groups [25, 26]. Experimental results showed that no NW could be obtained on the Si substrates in the absence of Au. This indicated that the presence of Au enhanced the growth of NWs and that the simultaneously anisotropic growth of GaN crystal is unlikely to take place in our system. Investigation by TEM-EDX reveals that only Ga and Au could be detected from the catalytic bead, indicating the possibility of alloy formation. The result is consistent with the previous reports [26], all of which suggested the VLS growth mechanism through binary Au–Ga alloy formation. However, neither of the reports could detect the N signal, and, also, N has been reported to have a poor solubility in Au [26]; we suspect that the alloying stage, which is a critical stage of the standard VLS growth mechanism, could not achieve the final ternary phase of Au–Ga–N. Recently, Persson *et al* [27] proposed another growth mechanism, in which NWs can be

grown without the alloying state through the vapour–solid–solid (VSS) mechanism. Although our work seems not to follow their VSS mechanism due to the formation of Au–Ga alloy, it is worth considering the possibility of the catalytic growth of NWs by a surface diffusion process [27].

In addition, it is also quite intriguing to note that the Au seed particle is always smaller in diameter than the attached GaN NW (figure 5); at the same time, they are in proportion. For NWs grown by the standard VLS process, the diameter of the seed nanosphere is either larger or equal to the diameter of the growing NWs [25, 26]. In the present case, the growth of GaN did not seem to derive directly from the interior of a supersaturated Au–Ga–N alloy seed. More likely, the reaction between N and Ga occurred right at the interface between the GaN NW and the seed sphere. Based on our experimental results, we suggest that the growth pathway is likely that Ga and Au formed liquid alloy in the first stage, and then this binary Au–Ga alloy catalyzed Ga and NH_3 vapour to react and form GaN. Finally, the elongation took place as GaN continued to deposit on the growing tip via AuGa/GaN interface, as demonstrated by Yu *et al* [26]. It can be rationalized that the GaN prefers to condense at the existing liquid/solid (AuGa/GaN) interface, because less energy is required in this step compared to the creation of a new nucleation site. This step might be the controlling kinetic process toward diameter selectivity.

To explain the relation between the Au particle size and the diameter of the attached GaN NW (table 1), we propose a self-regulating growth model in which a NW with a smaller catalytic bead (model I) is preferred over that with a larger catalytic bead (model II). As stated above, we assume that (i) Ga is activated through the catalyst and the reaction takes place only at the AuGa/GaN interface, and (ii) NH_3 does not dissolve into the catalyst. Based on (i), Ga can dissolve into an Au NP through the whole surface of the particle. Hence, the in-coming rate of Ga (abbreviated R_{in}) is proportional to the surface area of the Au NP and can be expressed as $R_{\text{in}} = \alpha \cdot r_{\text{Au}}^2$, where r_{Au} is the radius of an Au NP, assuming that the NP is a sphere. In such a case, R_{in} is the same in both models. Regarding the formation of GaN, we first demonstrate model II, in which the Au droplet at the top of GaN NW is larger or equal in diameter to that of the NW (the schematic diagram in figure 7(b)). The reaction can take place due to the diffusion of nitrogen (NH_3) at the contact circumference between the catalytic bead and NW. This is a diffusion-limited process, since the nitrogen cannot dissolve in gold. Therefore, the forming rate of GaN is proportional to the radius of NW (r_{NW}) and can be expressed as $R_{\text{GaN,II}} = \delta r_{\text{NW}}$. In model I, in which the Au bead has smaller diameter than the NW diameter, the contact area (at the Au–GaN interface) is of negligible value. For simplicity, we can assume that the Au NP stands on the GaN as a full sphere (the schematic diagram in figure 7(a)), which means that NH_3 can react directly with the entire top surface (around the Au–GaN interface point), neglecting the small contribution of the diffusion process at the point of contact. Therefore, the forming rate of GaN (abbreviated as R_{GaN}) is $R_{\text{GaN,I}} = \beta r_{\text{NW}}^2$.

By plotting R_{in} and R_{GaN} versus a reduced length unit r ($=r_{\text{NW}}/r_{\text{Au}}$), it can be easily understood that steady growth can occur only in model I (figure 7(a)) while a divergent growth condition is found in model II (figure 7(b)). We should mention

Figure 7. Plots of Ga in-coming rate R_{in} and GaN growth rate (R_{GaN}) versus a reduced length unit (r_{NW}/r_{Au}), along with the schematic diagrams for (a) growth model I, where the radius of the catalytic bead (r_{Au}) is smaller than that of the NW (r_{NW}), and (b) growth model II, where r_{Au} is larger than r_{NW} . Each diagram shows both side and top views of the GaN NW (dotted) with Au NP (white) at the top.

that, in both models, there exists one crossover point, r_c , at which $R_{in} = R_{GaN}$; any fluctuation from this point could cause either focus back to the steady growth at r_c or divergence to uncontrolled growth. In model II (figure 7(b)), for $r < r_c$, one has $R_{in} < R_{GaN,II}$; the growth of NWs will be under an unstable situation for shrinking, because, if $R_{GaN,II}$ is larger than R_{in} , the reaction will be quenched immediately due to the lack of Ga source. For $r > r_c$, one has $R_{in} > R_{GaN,II}$, so that the catalytic bead will grow continuously bigger and bigger and the NWs will be under an unstable situation for growth. In short, the growth will diverge from the equilibrium point (r_c) if $R_{in} \neq R_{GaN,I}$ in model II. On the other hand, in model I (figure 7(a)), no matter if $r > r_c$ or $r < r_c$ at the initial stage, the growth of NWs converges to r_c (where $R_{in} = R_{GaN,I}$). For $r < r_c$, $R_{in} > R_{GaN,I}$, more Ga will dissolve into the Au–Ga alloy bead; excess Ga will be separated out and will take part in the GaN growth reaction; and $R_{GaN,I}$ will increase towards the equilibrium point (r_c). Beyond r_c ($r > r_c$), one has $R_{in} < R_{GaN,I}$ or faster Ga consumption, which will slow down the reaction (or $R_{GaN,I}$) and the condition will tend to return at r_c . Therefore, we can consider that the steady growth model (model I) is preferable for the growth pathway of our GaN NWs. Same self-regulating growth mechanism in model I can also explain the size-selective phenomena. The convergence of growth towards a certain critical point r_c means that there always exists a r_{NW} for a certain r_{Au} , for a particular growth system. At least we can claim to have a steady growth condition from the evidence that the diameter of our GaN NWs

does show a deterministic relation (2.4) to the starting Au NP size. However, we are not able to account for the physical interpretation of the rate constants α , β and δ precisely at this stage, and that is the reason why we are unable to conclude any numerical value for the critical or equilibrium point r_c . Further experiments are underway.

4. Conclusion

In summary, we have demonstrated that solution-mono-dispersed Au NPs of distinct sizes on the ligand (MPTPS) modified substrate can be used to catalyze the large-scale, diameter-selective growth of GaN NWs. The narrowest diameter that we can obtain is around 10 nm. An interesting observation has been found that the diameter of the Au NP at the top of GaN NW is always smaller but proportional to the diameter of the corresponding GaN NW. The growth may involve a self-regulating size-control kinetic pathway, somewhat different to the standard VLS mechanism. A possible mechanism for the growth process has been proposed to explain the unique observations.

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