Research Article

Effects of Precursor-Substrate Distances on the Growth of GaN Nanowires

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GaN nanowires were synthesized through the Ni-catalyzed chemical vapor deposition (CVD) method using Ga_2O_3/GaN mixtures as gallium sources, and precursor-substrate distances were investigated as the important factor for the growth of GaN nanowires. The microstructure, composition, and photoluminescence property were characterized by X-ray diffraction, field emission scanning electron microscopy, high-resolution transmission electron microscopy, and photoluminescence spectra. The results showed that single crystalline GaN nanowires with the diameter of about 90 nm and the length up to tens of micrometers had been grown thickly across Si (100) substrates with uniform density. Moreover, the variations of the GaN nanowire morphology, density, and size were largely attributed to substrate positions which would influence Ga precursor density in the carrier gas, the saturation degree of gaseous reactants, and the catalyst activity, respectively, in the fabrication of GaN nanowires by the vapour liquid solid mechanism.

1. Introduction

One-dimensional semiconductor nanostructures are emerging as versatile nanoscale building blocks for future nanotechnologies in terms of their innovative physical properties and potential applications in electronic and photonic nanodevices [1]. GaN, a robust wide band gap semiconductor, has attracted much attention for its novel optical, electrical, and mechanical properties [2]. GaN nanowires have also shown great potential applications in nanodevices, such as blue light emitting diode [3], short-wavelength ultraviolet nanolaser [4], field effect transistor [5], Schottky diode [6], and field emitter [7]. To date, a series of methods, such as laser ablation [8], carbon-nanotube-confined reactions [9], hydride vapor phase epitaxy [10, 11], metal organic chemical vapor deposition (MOCVD) [12–14], and chemical vapor deposition (CVD) [15, 16], have been utilized to synthesize GaN nanowires. Due to low cost and simplicity, the chemical vapor deposition has been way ahead of other methods reported in the literature, and different gallium sources such as Ga [17, 18], Ga_2O_3 [19, 20], GaN [21, 22], Ga_2O_3/Ga [12], and Ga/$GaCl_3$ [23] have been employed. Moreover, it was found that mixed source materials are much better for the growth of GaN nanowires than the single gallium source. Ga bulk and Ga_2O_3 powder cannot be uniformly mixed [12], and $GaCl_3$ is deliquescent in air and needs to be operated in particular device [23]. Fortunately, the study showed that Ga_2O_3 and GaN powder could be mixed uniformly and they were not deliquescent in air. Meanwhile, the mixed gallium source can also provide high and stable gallium density in the carrier gas during the reaction. Thus, it is attractive to use the Ga_2O_3/GaN mixtures as the gallium source for the fabrication of high quality GaN nanowires through the CVD process. In addition, although there are reports about effects of precursor-substrate distances on the synthesis of nanowires [24], these researches did not explore

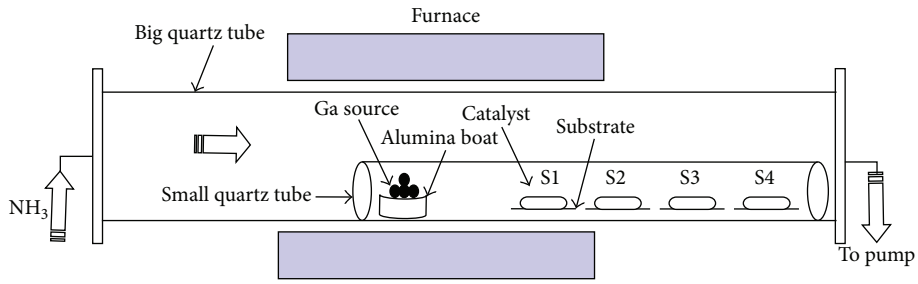

Figure 1: Schematic apparatus for the synthesis of GaN nanowires.

in detail the best position for the CVD growth of GaN nanowires. Therefore, investigation of effects of precursor-substrate distances on the growth of GaN nanowires, whereby a simple and repeatable process for the large fabrication of high quality GaN nanowires still has considerable appeal.

In this paper, GaN nanowires were synthesized on Ni-coated Si substrates via the CVD method. Ga_2O_3/GaN mixtures as the gallium sources and the substrate positions were investigated as the important factors for the growth of GaN nanowires. The microstructure, composition, and photoluminescence property were characterized by X-ray diffraction, field emission scanning electron microscopy, high-resolution transmission electron microscopy, and photoluminescence spectra. The results showed that substrate positions had important influence on the controllable fabrication of GaN nanowires by the vapour liquid solid mechanism.

2. Experimental

GaN nanowires were grown by the CVD process at 1100°C. Figure 1 shows the schematic apparatus for the synthesis of GaN nanowires. In the experiment, a layer of Ni catalyst (3 nm thick) was thermally evaporated onto a Si (100) substrate. The substrates were cleaned by the ultrasonic cleaning machine with acetone, ethanol, and deionized water for 30 min in sequence. After baking, the substrates were employed for the synthesis of nanowires. The alumina boat containing 0.1172 g gallium source and the substrate were put into a small quartz tube sequentially. Then, the small quartz tube was placed in a tube furnace (Lindberg blue, Thermo Scientific, Waltham, MA, USA) where the alumina boat was located in the center. The tube furnace was evacuated and flushed with Ar for 10 min and ramped at 30°C/min to the growth temperature (1100°C) in the flowing Ar atmosphere (20 sccm, standard cubic centimeters per minute). 30 sccm NH_3 was introduced instead of Ar after the temperature reached 1100°C and the furnace was kept at the growth temperature for 30 min. Finally, the system cooled down to room temperature in the Ar environment.

Four samples were prepared according to the different precursor-substrate distances (sample S1: 10 cm, sample S2: 11 cm, sample S3: 12 cm, and sample S4: 13 cm) from the gallium source. The surface morphology, microstructure, and composition of the GaN nanowires were characterized by scanning electron microscopy (SEM, FEI Quanta FEG), transmission electron microscopy (TEM, FEI Tecnai G2), high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2), and X-ray diffraction (XRD, Bruker D8 Advance Cu-Kα). Room temperature photoluminescence (PL) spectra were carried out by using 325 nm He–Cd laser as the excitation source.

3. Results and Discussion

Figure 2 shows the representative SEM images of grown samples. Long and straight GaN nanowires were largely synthesized using Ga_2O_3/GaN mixtures as gallium sources on the Si substrates. It is also interesting to note that the physical aspects of the synthesized GaN nanowires were significantly different for substrate positions (10 cm, 11 cm, 12 cm, and 13 cm) as shown in Figures 2(a), 2(b), 2(c), and 2(d). For sample S1, there are no nanowires but only some stacking structures. For sample S2, long and straight GaN nanowires with the length up to tens of micrometers were grown thickly across the whole substrate with uniform density. For sample S3, most of the GaN nanowires were zigzag with distorted shape. As for sample S4, the diameter of nanowires was nonuniform with stack surface. Thus, GaN nanowires grown at the substrate position of 11 cm have smooth surface and straight morphology, much better than other positions. Based on the SEM results, the precursor-substrate distances seem to have big influences on the surface morphology and microstructure of grown GaN nanowires.

X-ray diffraction (XRD) spectra of the GaN nanowires for four samples are shown in Figure 3. The peak intensity of substrate Si is too strong and has been omitted in order to clearly display other peaks in the XRD diagram. All the peaks (100), (002), (101), (102), (110), and (103) can be indexed to the hexagonal wurtzite structure of GaN with lattice constants of $a = 0.319$ nm and $c = 0.519$ nm, same as the standard card (JCPDS 76-0703). Moreover, Ga_2O_3 peaks are not present in the original diffraction peaks of XRD. With comparison of XRD spectra for the different substrate positions, the intensity of three major GaN peaks (100), (002), and (101) in sample S2 was stronger than that in samples S1, S3, and S4. The result indicates that the crystalline quality of nanowires grown by the substrate positions of 11 cm is significantly improved which is consistent with the above SEM analysis.

Further structural characterization of samples S2 and S3 was performed by TEM and high-resolution TEM (HRTEM)

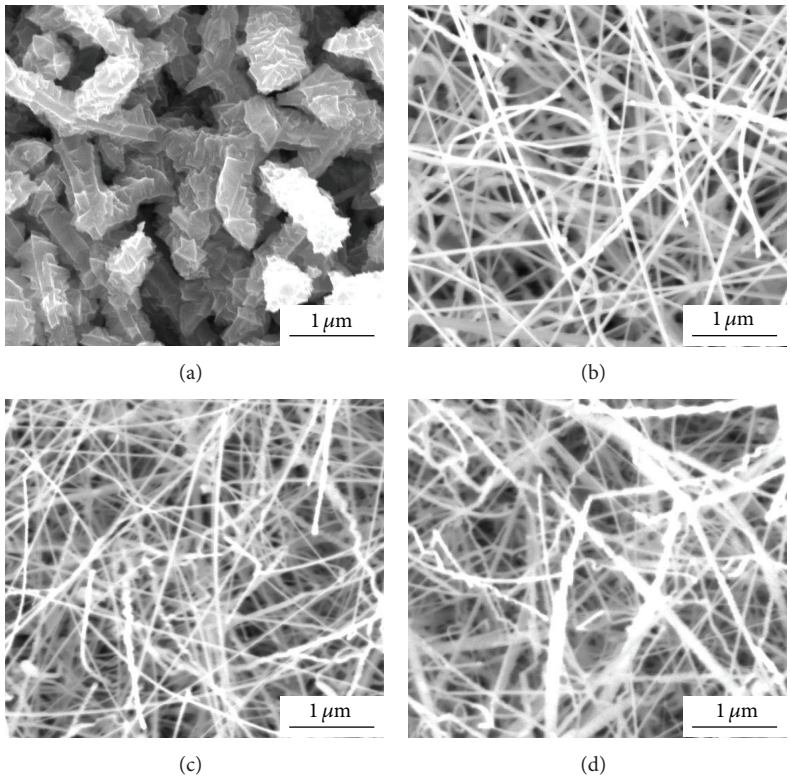

Figure 2: SEM images of samples (a) S1, (b) S2, (c) S3, and (d) S4.

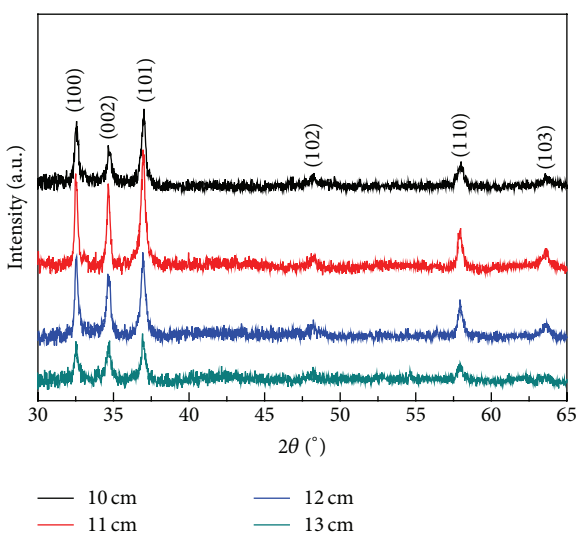

Figure 3: The XRD spectra of samples S1, S2, S3, and S4.

as depicted in Figure 4. S1 and S4 are not investigated due to their poor SEM results. Figure 4(a) shows the lower-amplified TEM image of sample S2, a single nanowire with a diameter of about 90 nm, which is straight and smooth. Figure 4(b) shows the HRTEM lattice image of sample S2; the visible lattice fringes illustrate that the nanowire is single crystal in nature. The interplanar spacing accurately measured is 0.24 nm, which corresponds to the (101) plane of hexagonal GaN. Figures 4(c) and 4(d) are images of sample S3. The straight nanowire with a diameter of about 60 nm is shown in Figure 4(c). Based on the HRTEM image (Figure 4(d)), the interplanar spacing accurately measured is 0.276 nm, which corresponds to the (100) plane of hexagonal GaN. Those conclusions are also consistent with the XRD results.

The growing procedures of GaN nanowires with different substrate positions are schematically illustrated in Figure 5. NH_3 decomposes to NH_2, NH, H_2, and N successively when ammoniating temperature is above 850°C [25]. The Ga_2O_3 particles are reduced to gaseous Ga_2O by H_2 and then GaN molecules are synthesized through the reaction of Ga_2O and ammonia [26]. When the temperature rises to 1000°C, GaN begins to decompose the raw Ga species and react with NH_3 to generate GaN [24]. Meanwhile, it is noted that a single Ga_2O_3 source produces low gallium density in the carrier gas during the heating process, which will result in uneven or disorder growth of nanowires. When only GaN is used as the gallium source, GaN starts to break down to generate Ga and nitrogen in the nitrogen atmosphere at 1050°C; however, the decomposed Ga species are evaporating fast which is a disadvantage for continual growth of nanowires. While the Ga_2O_3/GaN mixtures are exploited, Ga_2O_3 is first broken down to generate Ga_2O when the temperature is higher than 850°C, and GaN nanowires can be gotten by ammoniation. After the temperature further increases to 1000°C, GaN will decompose Ga species into the carrier gas which will improve the Ga density to help synthesize GaN nanowires during

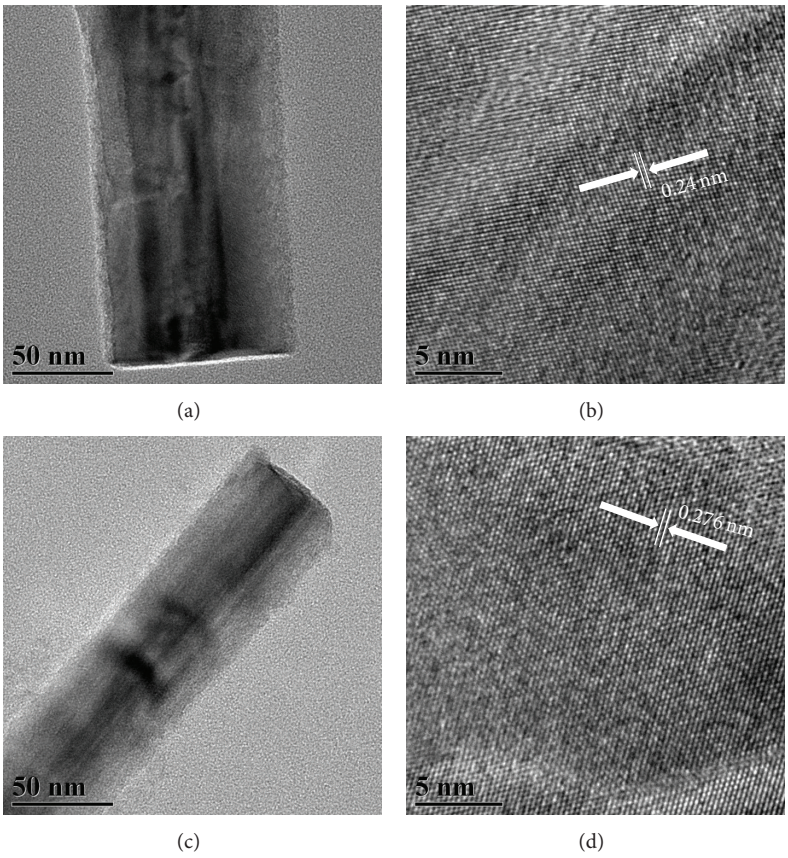

Figure 4: TEM (a) and HRTEM (b) images of sample S2. TEM (c) and HRTEM (d) images of sample S3.

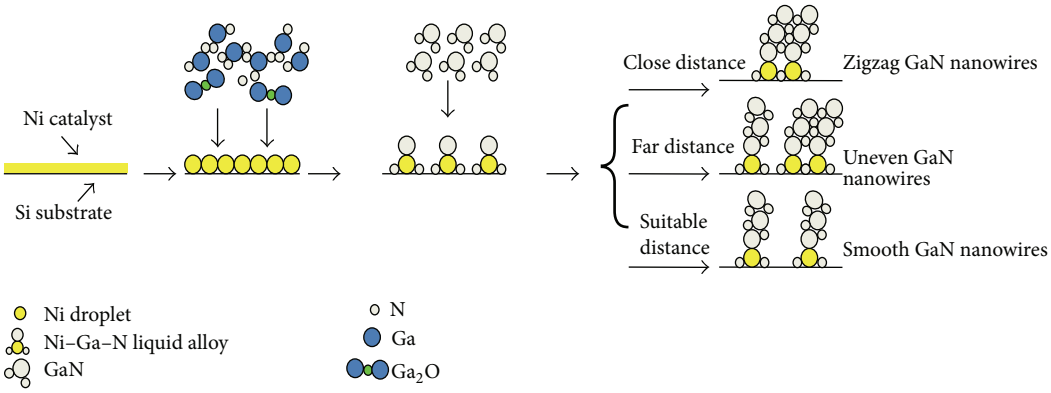

Figure 5: Schematic model illustrating the GaN nanowires growth with different distances.

the reaction. Based on the vapour liquid solid (VLS) mechanism, the Ni–Ga–N alloy droplets are formed on the substrate as nucleation sites for the growth of GaN microwires. When the concentration of the Ga–N flux exceeds the saturation point within the Ni–Ga–N droplets, GaN nanowires are obtained [26, 27]. Here the saturation degree of gaseous reactants and the catalyst activity are highly dependent on the substrate position [24]. As the substrate is 10 cm away from the gallium source where the temperature is about 980°C, a large number of stacking and disordered nanostructures are formed in a short period of time due to the fast precipitation nucleation speed. As the substrate is 11 cm away from the gallium source with the temperature of about 950°C, the gas flow, reaction temperature, and gas concentration are most suitable for the nucleation and growth. However, as the distance increases to 12 cm with the temperature of 930°C, the catalyst activity and the concentration of the reactant species decrease. Thus, the slow reaction rate results in the instable and uneven growth. As the location is farther away from the gallium source, the growing condition is worse for

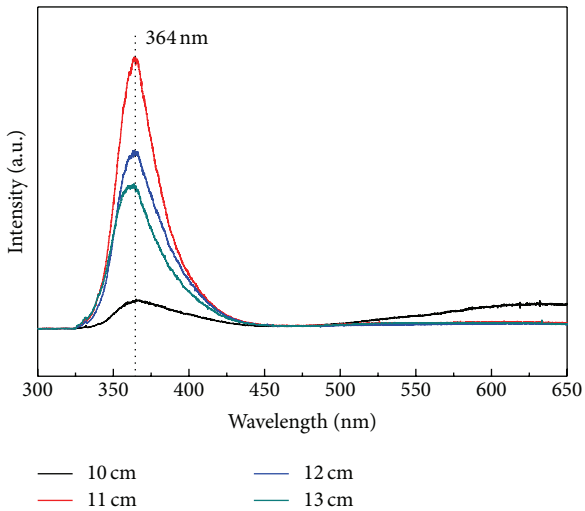

Figure 6: Room temperature PL spectra of samples S1, S2, S3, and S4.

the formation of GaN nanowires, and even a small amount of film is deposited on the substrate. As a result, the substrate position has great influence on the growth of GaN nanowires.

A 325 nm He–Cd UV laser was used as the excitation light source, and typical room temperature PL spectra for GaN Nanowires are illustrated in Figure 6. The band-edge emission peaks for all four samples are located at the wavelength of 364 nm which were caused by the interband transition [20]. When the distance between the substrate and the gallium source increased from 10 cm to 13 cm, the emission peak almost kept the same position, but the intensity gradually changed and reached the highest value at a distance of 11 cm. Therefore, the substrate positions have great influence on the optical properties of GaN nanowires. For 11 cm samples, the emission peak caused by the interband transition is strong and narrow, and no other luminescence peak was induced by impurities and defects, indicating that high crystalline GaN nanowires have been synthesized via the CVD method. Moreover, for 10 cm samples an emission peak at the wavelength of 620 nm was found which might be due to the Ga and N vacancies in GaN crystals [28].

4. Conclusions

GaN nanowires were successfully synthesized on Ni-coated Si (100) substrates using Ga_2O_3/GaN mixtures as gallium sources. With the substrate position 11 cm away from the gallium source, single crystalline GaN nanowires with the diameter of about 90 nm and the length up to tens of micrometers had been grown thickly across the substrate with uniform density. It is also found that substrate positions have large effects on Ga precursor density in the carrier gas, the saturation degree of gaseous reactants, and the catalyst activity, respectively, in the fabrication of GaN nanowires by the vapour liquid solid mechanism.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Authors' Contribution

Hongbin Cheng and Jia Li contributed equally to this work.

Acknowledgments

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