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Synthesis of large-scale GaN nanowires by ammoniating Ga_2O_3 films on Co layer deposited on Si(111) substrates*

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A mass of GaN nanowires has been successfully synthesized on Si(111) substrates by magnetron sputtering through ammoniating Ga_2O_3/Co films at 950°C. X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscope and Fourier transformed infrared spectra are used to characterize the samples. The results demonstrate that the nanowires are of single-crystal GaN with a hexagonal wurtzite structure and possess relatively smooth surfaces. The growth mechanism of GaN nanowires is also discussed.

Keywords: nanowires, crystal growth, scanning and transmission electron microscopy
PACC: 6146

1. Introduction

Wurtzite structure gallium nitride (GaN) is an important semiconductor material in optoelectronic applications due to its large direct band gap (E_g = 3.4 eV at 300 K), high thermal stability and strong resistance to radiation.[1−6] One-dimensional nanostructure, GaN nanowire, has lately attracted much attention because of its potential for microelectronic device. Many research groups have succeeded in synthesizing the GaN nanowires or nanorods by using various methods such as carbon-nanotube-confined reaction,[7] arc discharge,[2] sublimation,[3] laser ablation,[8] and chemical vapour deposition.[9−11] It is one of important research directions to synthesize the GaN nanostructures with the existence of some metal catalysts such as Fe, Ni, Au and so on. It was reported that GaN nanostructures were obtained by using Au,[3] Fe,[12] Ni[13] and In[14] as catalysts. In this paper, we report that we have successfully synthesized large-scale GaN nanowires through ammoniating the sputtered Ga_2O_3 films with the catalysis of Co on Si(111) substrates and briefly discussed the growth mechanism. We also deposit Ga_2O_3 films directly onto Si substrates under the same conditions, but no nanowires are formed. This growth method allows a continuous synthesis and produces a large quantity of single-crystalline GaN nanowires with a relatively high purity but at a low cost. Therefore, it is likely to be of interest for commercial-scale production.

2. Experiments

Firstly, silicon substrate was ultrasonic cleaned in absolute ethyl alcohol, and de-ionized water for 30 min in sequence. Secondly, the Co films with a thickness of about 20 nm were deposited on Si substrates by sputtering a Co target with a purity of 99.99% for 30 s with JCK-500A radio frequency magnetron sputtering. The background pressure of the sputtering chamber was about 5.5×10^{-4} Pa, and Ar with a purity of 99.999% under a pressure of 2 Pa was introduced into the chamber as the sputtering gas. The distance between the target and the substrate was 8 cm. Under the same conditions, the Ga_2O_3 with a purity of 99.999% thin films with a thickness of about 500 nm were grown on the Co-coated Si substrates by sputtering a sinter Ga_2O_3 target for 90 min. Finally, the Ga_2O_3/Co films were ammoniated under a flowing ammonia atmosphere with a flow rate of 500 ml/min in a horizontal tube furnace. The ammoniating was carried out at a temperature of 950°C for 15 min. After reaction, a light-yellow layer was found to be deposited on the substrate surface.

We have studied the structure, morphology, composition and optical properties of the samples using x-ray diffraction (XRD, Rigaku D/max-rB Cu

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Kα), scanning electron microscopy (SEM, Hitachi S-570), high resolution transmission electron microscope (HRTEM, Philips Tecnai F30), and Fourier transformed infrared spectra (FTIR, TENSOR27).

3. Results and discussion

Figure 1 shows the XRD pattern of the sample deposited on a Si substrate, in which the diffraction peaks located at $2\theta = 32.2°$, $34.4°$, $36.7°$ and $48.0°$ correspond to (100), (002), (101) and (102) planes of GaN, respectively, demonstrating that the reflections can be indexed to the hexagonal GaN phase with the lattice constants $a = 0.318$ nm and $c = 0.518$ nm, which are consistent with the reported values of bulk GaN.[15] There are no peaks of impurities appearing in the spectra, suggesting the predominant single wurtzite GaN phase of the deposit.

Figure 2 shows SEM images of the sample grown on the Co-deposited silicon substrate. Figure 2(a) indicates that the light-yellow layer is composed of high-density GaN nanowires, crossed each other and homogeneously distributed on the whole surface of Si substrate. The magnified SEM images (Figs.2(b) and 2(c)) shows that the majority of the nanowires are grown with a diameter of about 150 nm and a length of up to 10 μm and the surfaces of nanowires are smooth and clean without any particle impurities.

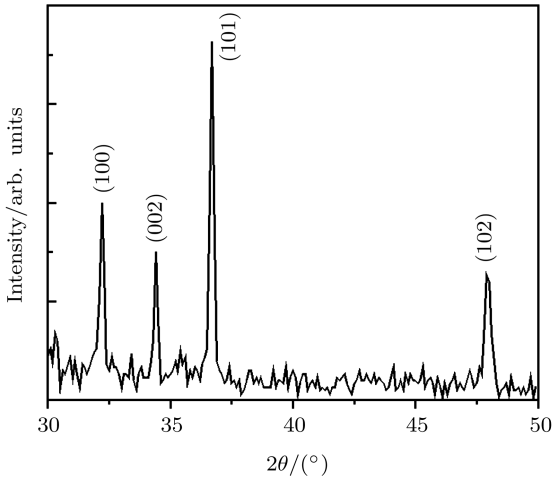


Fig.1. XRD pattern of as-synthesized GaN nanowires.

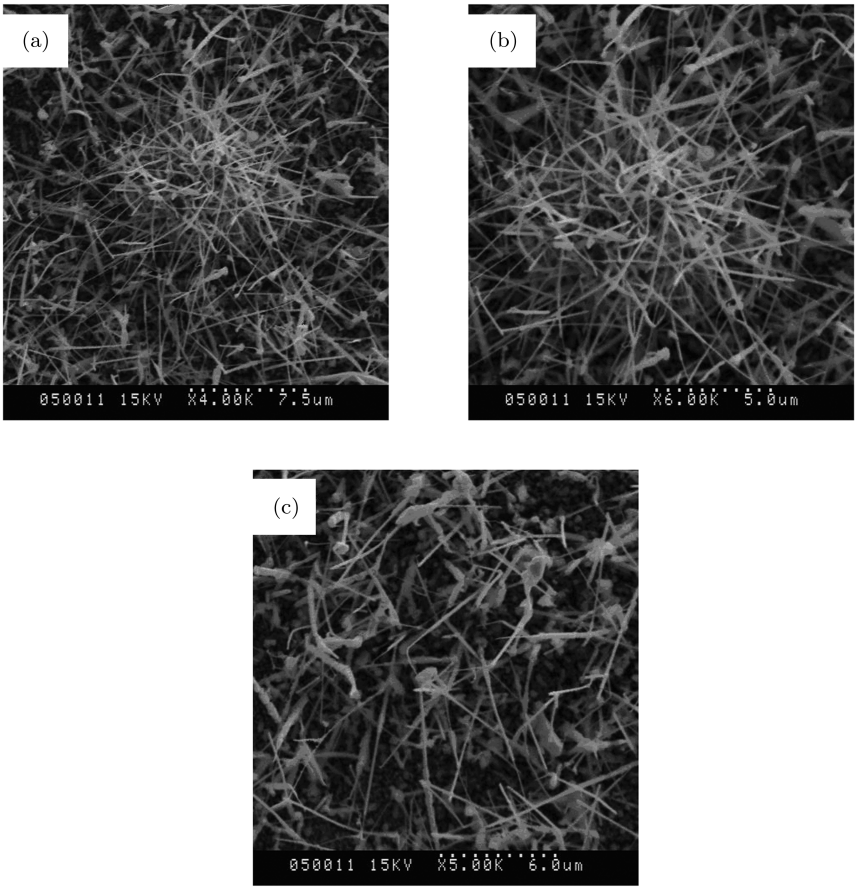


Fig.2. SEM image of GaN nanowires.

High-resolution TEM (HRTEM) (Fig.3) was carried out to further understand the structural properties of the nanowires. Figure 3(a) shows the high-resolution TEM (HRTEM) image of individual GaN nanowire with a diameter of approximate 200 nm, which is very straight and smooth on the surface. The inset shows its corresponding selected-area electron diffraction (SAED) pattern, which can be indexed to the diffraction of wurtzite GaN crystal along the $[1\bar{2}1\bar{3}]$ direction. Atomic-resolved view reveals negligible defects in the lattice planes [Fig.3(b)]. The visible lattice fringes illustrate that the nanowire is of high-quality single-crystal in nature. The closest interplanar distance was measured to be 0.2762 nm corresponding to that of the crystal plane (100) of GaN, indicating that the growth direction of the nanowire is perpendicular to the (100) plane, which is in accordance with the XRD result. All of the nanowires, we observed, are grown with the same structure.

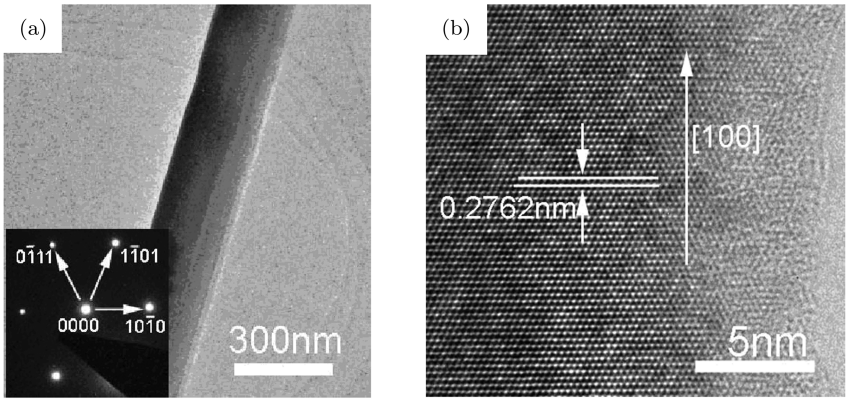


Fig.3. HRTEM image and SAED pattern for a single crystal-crystalline GaN nanowire (a) and atomic-resolved view (b) of the selected region of (a).

Figure 4 shows the FTIR transmission spectrum of the GaN nanowires synthesized at 950°C. The absorption of infrared radiation causes the various bands in a molecule to stretch and bend with respect to one another.[16] In the infrared spectrum, the transverse optical phonon mode appears in the form of an absorption band. Our infrared spectrum for GaN nanowires ammoniated at 950°C shows an absorption band at 563.88 cm^{-1}, corresponding to the E_2 (high) phonon mode of GaN, which is consistent with the previous Raman scattering study.[17] Another sharp absorption band at 607.37 cm^{-1} is due to the local vibration of the substitutional carbon in the Si substrate crystal lattice.[18] The absorption band located at 1105.13 cm^{-1} should be attributed to the Si-O-Si asymmetric stretching vibration in the SiO_2 resulting from oxygenation of Si substrate.[19]

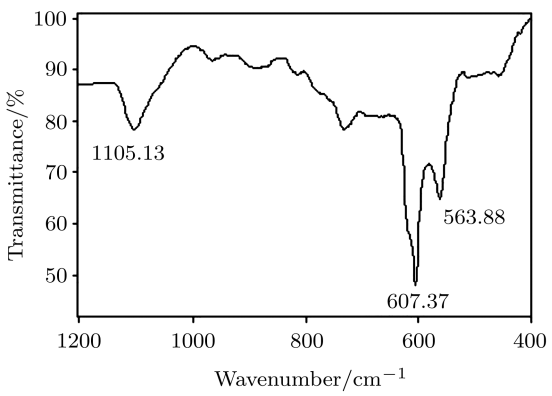


Fig.4. FTIR spectra of the GaN nanowires ammoniated at 950°C.

Based on the above analysis, the growth process can be described as follows. Since the fluidization temperature of nanosized catalytic metal particles is lower than that of bulk metal,[20] liquid Co droplets are formed at a reaction temperature on the Si surface. At the same time, NH_3 decomposes stepwise into NH_2, NH, H_2 and N when ammoniating temperatures are above 850°C.[21,22] The Ga_2O_3 particles are reduced to gaseous Ga_2O by H_2 and then GaN molecules are synthesized through the reaction between Ga_2O and ammonia. All the reactions can be expressed as follows:

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g), \quad (1)$$

$$Ga_2O_3(s) + 2H_2(g) \rightarrow Ga_2O(g) + 2H_2O(g), \quad (2)$$

$$Ga_2O(g) + 2NH_3(g) \rightarrow 2GaN(s) + 2H_2(g) + H_2O(g). \quad (3)$$

Subsequently, the supplied gaseous Ga and N are absorbed by Co droplet to form a kind of Co–Ga–N transition alloy droplet, as shown in Fig.5. When the concentration of GaN exceeds a saturation point of the Co–Ga–N alloy, GaN begins to grow from the alloy droplet and agglomerate into micrograins. When the growth directions of the micrograins are oriented to the same direction, the single GaN nanowires are formed. The Ga_2O_3 films are also deposited directly onto Si substrates under the same conditions, but no GaN nanowires are formed. It can be concluded that the high temperature, ammonia, Co layer and Ga_2O_3 are crucial for the growth of GaN nanowires. The size and the shape of Co droplets and the saturation of GaN vapour are presumably dominant factors to the morphology and crystallinity of GaN nanowires. However, the further role the Co layer plays in growing GaN nanowires needs more detailed investigation.

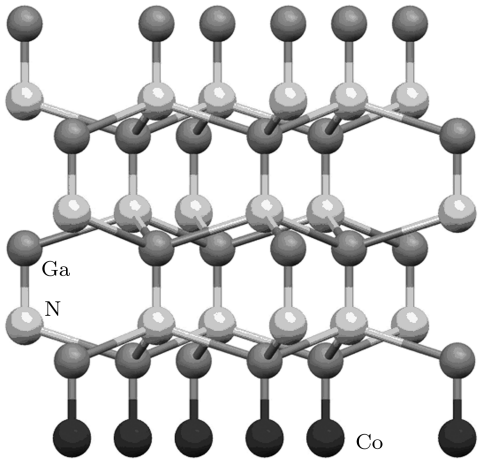


Fig.5. Growth mechanism model of a GaN nanowire.

4. Conclusion

High-density GaN nanowires with a diameter of around 150 nm and a length of up to 10 μm have been synthesized on the Si(111) substrate using Co as a catalyst. Most of the nanowires are of single-crystalline wurtzite GaN crystals grown along the [100] direction. The GaN nanowires grow with the help of a kind of Co–Ga–N transition alloy droplet.

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