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Synthesis and Characterization of GaN Nanorods by Ammoniating Ga_2O_3/Co Films Deposited on Si(111) Substrates*

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Abstract: GaN nanorods are successfully synthesized on Si(111) substrates with magnetron sputtering through ammoniating Ga_2O_3/Co films at 950℃. X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and Fourier-transform infrared spectroscopy are used to characterize the samples. The results demonstrate that the nanorods are single-crystal GaN with a hexagonal wurtzite structure and possess relatively smooth surfaces. The growth mechanism of GaN nanorods is also discussed.

Key words: nanorods; crystal growth; scanning and transmission electron microscopy
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1 Introduction

As a third generation semiconductor, gallium nitride (GaN) has attracted much attention as a material for short wavelength optical devices and high power electron devices because of its excellent optical and electrical properties[1,2]. GaN is a very important and useful semiconductor material due to its wide and direct band gap (3.4eV at 300K), high thermal stability, and strong resistance to radiation[3~5]. In recent years, a considerable amount of work has been done to study GaN nanowires[6,7]. In 1997, Han *et al*. employed carbon-nanotube-confined reaction to fabricate the GaN nanowires[7]. In addition, various techniques, such as the laser ablation method[9], the oxide-assisted method[10], chemical vapor deposition[11], and pulsed laser deposition[12] were applied to synthesize GaN nanowires. Compared to these techniques, radio frequency magnetron sputtering is a newer method for the growth of the seed layers[13]. It was reported that some metal catalysts have been used for nanostructures growth, such as Fe[14], Ni[15] and Au[5].

In this work, Co films were deposited on the substrates as the interval layer and high purity Ga_2O_3 target (purity: 99.999%) was applied as Ga source. The GaN nanorods were grown by ammoniating Ga_2O_3/Co thin films deposited on Si(111) substrates with radio frequency magnetron sputtering. To our knowledge, no experimental study has been done on the GaN nanorods with this method. This growth method allows a continuous synthesis and produces large-scale, single-crystal GaN nanorods at relatively high purity and low cost.

2 Experiment

As mentioned above, we reported ammoniating reaction synthesis of the GaN nanorods using Ga_2O_3/Co films deposited on Si(111) substrate in flowing ammonia. First, silicon substrate was ultrasonically cleaned in absolute ethylalcohol and de-ionized water for 30min in sequence. Second, thin Co films of about ten nanometers were deposited on Si substrates by sputtering a Co target (purity: 99.99%) for 10s with JCK-500A radio frequency magnetron sputtering. The background pressure of the sputtering chamber was about 5.5×10^{-4} and Ar (purity: 99.999%) under 2Pa pressure was introduced into the chamber as the sputtering gas. The distance between the target and the substrate was 8cm. Under the same conditions, Ga_2O_3 (purity: 99.999%) thin films were grown on the Co-coated Si substrates by sputtering a sinter Ga_2O_3 target for 90min. Finally, the Ga_2O_3/Co films were ammoniated under flowing ammonia atmosphere with a flow rate of 500ml/min in a horizontal tube furnace. The temperature of the ammoniating was 950℃ and the duration was 20min. After reaction, a deposit of light-yellow layer was found on the substrate surface.

We studied the structure, morphology, composition, and optical properties of the samples using X-ray diffraction (XRD, RigaKu D/max-rB CuKα), scanning electron microscope (SEM, Hitachi S-570), high-resolution transmission electron microscopy (HR-

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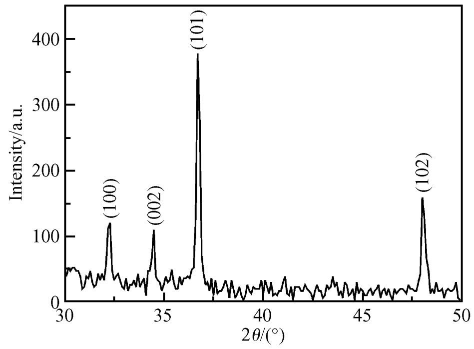

Fig. 1　XRD pattern of as-synthesized GaN nanorods

TEM, Philips Tecnai F30), and Fourier transform infrared spectroscopy (FTIR, TENSOR27).

3　Results and discussion

Figure 1 shows the XRD pattern of the sample deposited on Si substrate. The diffraction peaks in the panel are at $2\theta = 32.2^\circ, 34.4^\circ, 36.7^\circ$, and 48.0° corresponding to the (100), (002), (101), and (102) planes of GaN, respectively. 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[16]. Moreover, no other peaks of impurities appear in the spectra, indicating the predominant single wurtzite GaN phase of the deposit and the sharp diffraction peaks reveal that the GaN nanorods possess good crystalline quality.

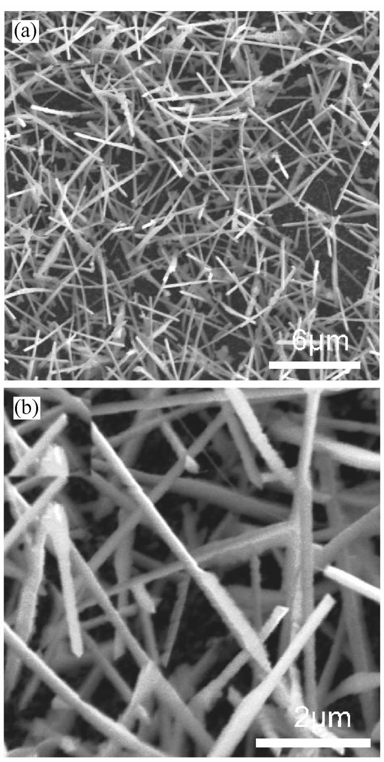

Fig. 2　SEM image of GaN nanorods (a) and the magnified image (b)

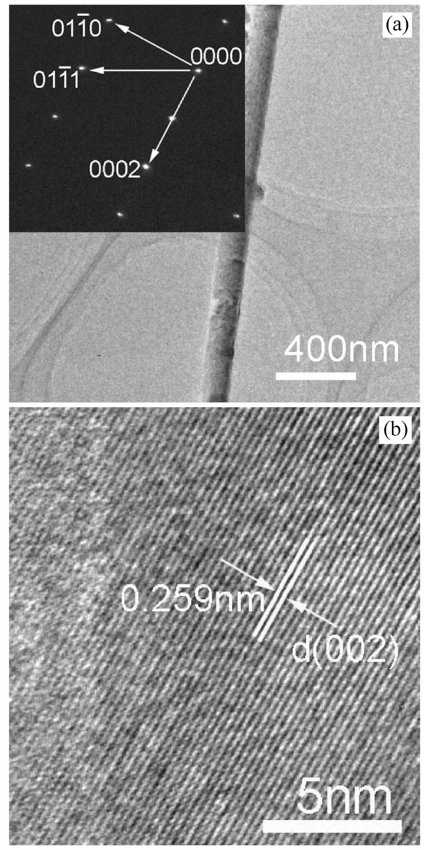

Fig. 3　(a) HRTEM image and SAED pattern for a single crystal-crystalline GaN nanorod; (b) Atomic-resolved view of the selected region of (a)

Figure 2 shows the SEM images of the sample grown on the Co-deposited silicon substrate. Figure 2 (a) shows that the light-yellow layer is composed of high-density GaN nanorods, crossing each other and homogeneously distributing over the whole surface of Si substrate. A magnified SEM image (Fig. 2 (b)) shows that the majority of the nanorods are grown with a diameter of about 150nm and a length up to ten microns and the surface of nanorods is smooth and clean without any particle impurities.

High-resolution TEM (HRTEM) (Fig. 3) was carried out to further understand the structural properties of the nanorods. Figure 3 (a) shows the high-resolution TEM (HRTEM) image of an individual GaN nanorod with a diameter of approximately 160 nm, which is very straight and smooth on the surface. The inset is its corresponding selected-area electron diffraction (SAED) pattern, showing the GaN crystal of single-crystalline wurtzite structure and the growth direction parallel to the [010] direction of the hexagonal unit cell. The atomic-resolved view reveals negligible defects in the lattice planes (Fig. 3 (b)). The visible lattice fringes illustrate that the nanorod is naturally a high-quality single-crystal. The interval of closest interplanar distance was measured to be

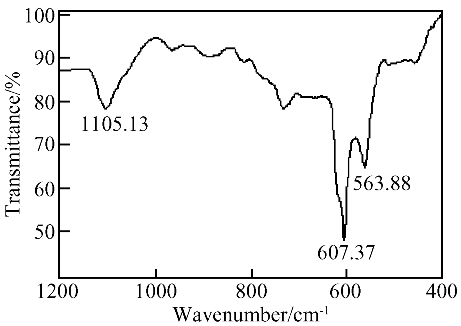

Fig.4 FTIR spectrum of the GaN nanorods ammoniated at 950℃

0.259nm, corresponding to that of the crystal plane (002) of GaN, which is in accordance with the XRD result. All of the nanorods we observed had the same structure.

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

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 reaction temperature on the Si surface. At the same time, NH_3 decomposes stepwise to NH_2, NH, H_2, and N when the ammoniating temperature is above 850℃[21]. 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. These 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 a Co droplet to form a Co-Ga-N transition alloy droplet, as observed in the model of Fig.5. When the concentration of GaN exceeds the saturation point of the Co-Ga-N alloy, GaN begins to grow

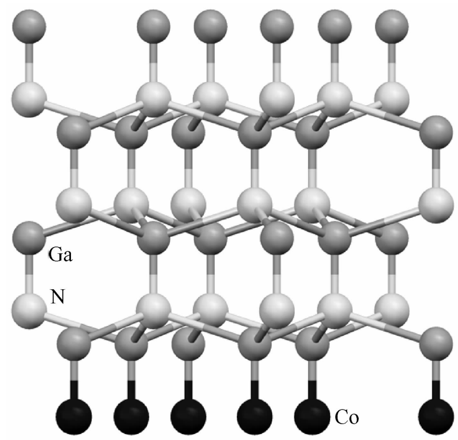

Fig.5 Growth mechanism model of a GaN nanorod

from the alloy droplet and agglomerate into micrograins. When the growth directions of the micrograins are oriented in the same direction, the single GaN nanorods are formed. The Ga_2O_3 films are also deposited directly onto Si substrates under the same conditions, but no GaN nanorods are formed.

Therefore, high temperature, ammonia, the Co layer, and Ga_2O_3 are crucial to the growth of the GaN nanorods. The size and shape of the Co droplets and the saturation of GaN vapor are presumably the dominant factors in the morphology and crystallinity of the GaN nanorods. However, more investigation is needed on the function of the Co layer in the growth of the GaN nanorods.

4 Conclusion

In summary, high-density GaN nanorods were synthesized on Si(111) substrates using Co as the catalyst. The diameter is around 150nm and the length is several microns. Most of the nanorods are single-crystalline wurtzite structured GaN crystals grown along the (010) direction. We hope our work will help to devise nanoscale electronic and photonic devices.

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氨化 Si 基 Ga_2O_3/Co 薄膜合成 GaN 纳米线及其表征*

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摘要：采用磁控溅射技术先在 Si 衬底上制备 Ga_2O_3/Co 薄膜，然后在 950℃ 下流动的氨气中进行氨化反应制备 GaN 纳米棒．应用 X 射线衍射、扫描电镜、傅里叶红外吸收光谱、选区电子衍射和高分辨透射电子显微镜对样品进行表征．结果表明，采用此方法得到了六方纤锌矿结构的 GaN 单晶纳米棒．观察发现纳米棒表面光滑．并讨论了 GaN 纳米棒的生长机制．

关键词：纳米棒；晶体生长；扫描和透射电子显微镜

PACC：6146；6110M；6116P

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