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Nitridation effects of Si(1 1 1) substrate surface on InN nanorods grown by plasma-assisted molecular beam epitaxy

Shan Feng [a], Jin Tan [a,b,*], Bin Li [a], Hao Song [a], Zhengbo Wu [a], Xin Chen [a]

[a] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China
[b] Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, China

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ABSTRACT

The InN nanorods were grown on Si(1 1 1) substrate by plasma-assisted molecular beam epitaxy (PAMBE) system, with a substrate nitridation process. The effect of nitriding time of Si(1 1 1) substrate on morphology, orientation and growth temperature of InN nanorods was characterized via scanning electron microscopy (SEM) and X-ray diffraction (XRD). The deviation angle of InN nanorods was measured to evaluate the alignment of arrays. The results showed that InN nanorods could not be formed with 1 min nitridation of Si(1 1 1) substrate, but they could be obtained again when the nitriding time was increased to more than 10 min. In order to get aligned InN nanorods, the growth temperature needed to increase with longer nitriding time. The vertical orientation of InN nanorods could be enhanced with increase in nitriding time. The influence of the substrate nitridation on the photoluminescence (PL) spectra of InN nanorods has been investigated.

1. Introduction

In recent years, InN has attracted much attention since its band gap had been reported to be 0.7–0.8 eV [1–6]. InN has the smallest effective electron mass of all the group-III nitrides, which gives rise to high carrier mobility, saturation velocity and a large drift velocity at room temperature. Meanwhile, alloying with GaN and AlN, it can cover the energy range from the near infra-red to ultra-violet region. These properties make InN a good candidate for optoelectronic devices, such as laser diodes, high efficiency solar cells and high frequency/high power electronic devices.

With the rapid progress in epitaxial growth techniques, plasma-assisted molecular beam epitaxy (PAMBE) and metal organic chemical vapour deposition (MOCVD) have been widely used to obtain high quality films, nanorods and quantum dots, leading to the applications such as light-emitting diodes (LEDs) [7,8], superluminescent light-emitting diodes (SLED) [9–11] and laser diodes [12]. Nanorod structures have distinct benefits compared to the conventional thin films, including defect-free and strain relaxation. InN nanorods have been successfully grown on different substrates including Si [13,14], sapphire [15], and SiC [16] by PAMBE and MOCVD. However, well-aligned and homogeneous InN nanorods are difficult to be grown on the substrate without buffer layer or metal catalyst, which restricts the research on fundamental properties of InN, severely limiting their device applications. In previous reports [17–19], when InN nanorods were grown on bare Si(1 1 1), a thin amorphous Si_xN_y layer would develop at the interface before the growth at a relatively low temperature (≈500 °C). And the amorphous Si_xN_y layer on Si(1 1 1) could make InN nanorods grow misoriented and tilted with respect to the substrate. On the other hands, Park et al. and Sakai et al. [20,21] found that the Si_xN_y buffer could be porous with many nanometer-sized holes under certain experimental conditions, which can act as a good template for low-temperature GaN layer.

In this report, we have performed a detailed investigation of the nitridation effect of Si(1 1 1) substrate surface on InN nanorods. The morphology evolution, structural and optical characterizations have been analyzed under different nitridation conditions. It was found that the nitridation of substrate has a strong effect on the morphology, orientation and growth temperature of InN nanorods.

2. Experimental

The InN samples were grown on Si(1 1 1) by PAMBE system equipped with a radio frequency plasma source (SVTA-RF-4.5PBN). Si(1 1 1) substrates were first chemically cleaned followed by dipping in 6% HF to remove the surface oxide layer. The substrates were then loaded into the MBE system and thermally cleaned at 900 °C for 1 h. Subsequently, the RF nitrogen plasma was switched on at 900 °C substrate temperature, forming a nitridation layer of amorphous Si_xN_y, while keeping the nitrogen flow rate and RF power at 0.7 sccm and 350 W, respectively. The

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* Corresponding author at: Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China. Tel.: +86 027 67884814.
E-mail address: jintan_cug@163.com (J. Tan).

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substrate nitriding time was varied within the range of 0–90 min. After nitridation, the substrate temperature was lowered for the growth of InN. The growth temperatures (T_{subs}) were varied within the range of 500–570 °C. The substrate nitriding time and substrate temperature of InN for investigated samples are given in Table 1. The growth time was 120 min for each sample. During the growth, the In cell temperature was kept at 800 °C and the corresponding beam equivalent pressure(BEP) was 1.5×10^{-7} mbar, while the nitrogen flow rate and RF power were 0.7 sccm and 350 W, respectively. In samples (a)–(f), the InN was grown at 500 °C and nitriding time was kept at 0, 1, 10, 30, 60, and 90 min, respectively. In samples (g)–(i), the InN was grown at 530, 550, and 570 °C while nitriding time was kept at 30, 60, and 90 min, respectively.

The morphology and structural characterizations of samples were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The SEM (Hitachi S-8010) measurements were carried out at 15 kV, 10 μA. The XRD (Bruker D8 Focus) measurements were characterized with Ni-filtered Cu Kα (λ = 1.540598 Å) radiation at 40 kV tube voltage and 40 mA tube current. The PL spectra were measured from 16 K to 300 K using a FLS920 fluorescence spectrometer (Edinburgh Instruments) equipped with a closed cycle helium cryostat and a Xe lamp of 488 nm excitation wavelength with a nominally input power of 500 mW.

3. Results and discussion

Fig. 1 shows the morphology evolution of InN nanorods in samples (a)–(f) grown on Si(1 1 1) substrate at 500 °C with different nitriding time. It is found that misoriented and tilted InN nanorods were grown on bare Si(1 1 1) substrate without nitridation process in Fig. 1(a). The nanorods were hexagonal with diameters and heights of ~36 nm and ~550 nm, respectively. When the nitriding time of Si(1 1 1) was 1 min in Fig. 1(b), the surface was a coarse grain structure showing a compact layer. But when the nitriding time increased to 10 min, nanorods were observed again with diameters and heights of ~35 nm and ~450 nm as shown in Fig. 1(c). In Fig. 1(d)–(f), with a further nitriding time from 30 min to 90 min, a high density of coalescent unfaceted nanorods was exhibited with shorter height as shown in Table 1. The growth temperature is understood to influence the diffusion of In adatoms along the sidewalls of nanorods [19]. At lower temperature, In diffusion length is shorter, easily leading to the coalesce and tapering toward the top. Fig. 2 illustrates the h/d ratio as a function of nitriding time and growth temperature. It shows that the h/d ratio decreased with the nitriding time rising to 30 min and then increased gradually with the nitriding time rising to 90 min at the same growth temperature of 500 °C.

The above results reveal that the size, shape and proper growth temperature of InN nanorods were greatly influenced with increase in Si(1 1 1) substrate nitriding time. Some reporters pointed out that, amorphous Si_xN_y could develop gradually on bare Si(1 1 1) before the growth of InN [17,18]. Thus, epitaxial relation got lost on the nitrided area, which resulted in misoriented nanorods or a coarse grain structure on Si(1 1 1). When the substrate nitriding time was longer than 10 min, we suspected that many holes may be formed, similar to the case of Si_xN_y grown on Si(1 1 1) [20], which could act as a template in our experiment to obtain nanorods. Therefore, InN nanorods could be observed again when the nitriding time was longer than 10 min.

Table 1
Substrate temperature (T_{subs}) and substrate nitriding time (t_{nitr}) employed in the growth process of the samples were studied in this work. The average height (h), diameter (d), and (h/d) ratio of the nanorods and the different morphologies observed are also summarized.

Sample	T_{subs} (°C)	t_{nitr} (min)	d (nm)	h (nm)	h/d	Morphology
a	500	0	36	550	15.27	Hexagonal
b	500	1				Layerlike
c	500	10	35	450	12.86	Hexagonal
d	500	30	35	180	5.14	Unfaceted
e	500	60	35	200	5.71	Unfaceted
f	500	90	45	280	6.22	Unfaceted
g	530	30	40	410	10.25	Hexagonal
h	550	60	50	500	10.00	Hexagonal
i	570	90	90	320	3.56	Hexagonal

In order to increase the diffusion of In atoms, the growth temperature was increased. Fig. 3 implies the morphology evolution of InN nanorods in samples (g)–(i). As the growth temperature rose to 530 °C after 30 min substrate nitridation, InN nanorods separated and grew higher in Fig. 3(g), while they were hexagonal and still misoriented to a certain degree with larger diameters and heights of ~40 nm and ~410 nm, respectively. But the proper growth temperature of 550 °C was needed to get separated InN nanorods after 60 min substrate nitridation as shown in Fig. 3(h). The diameters and heights further increased to ~50 nm and ~500 nm, respectively. Meanwhile, the coalescence of nanorods was not severe, resulting in homogeneous, hexagonal shaped nanorods perpendicular to the Si(1 1 1) substrate. With a longer nitriding time of 90 min in Fig. 3(i), a higher temperature of 570 °C was needed to get separated and hexagonal shaped InN nanorods. From the sample (i), we can see that the nanorods were well hexagonal and perpendicular to the substrate, but were tapering to pencil-shape at the growth front. The diameters and heights of nanorods further increased to ~90 nm and ~320 nm compared to sample (f), respectively. The h/d ratio of different samples was shown in Table 1 and Fig. 2. It is rather obvious, from Fig. 3, that the vertical orientation of InN nanorods was enhanced and the optimum growth temperature was improved with increase in substrate nitriding time. As the amorphous Si_xN_y layer got thicker with longer nitriding time, the holes were expected to get smaller and deeper, which was better for heteroepitaxy. Meanwhile, the consumption and diffusion both improved when the substrate temperature increased. Thus, better oriented and lager size of nanorods could be obtained with longer substrate nitriding time and higher growth temperature.

The deviation angle distributions of samples (g), (h), and (i) InN nanorods obtained from cross section SEM images and the percentage of vertical-aligned (θ = 0°) ones are analyzed. From Fig. 4, it can be seen that the InN nanorods mostly distribute in the range of 0–2°. It reveals a well epitaxy between Si(1 1 1) and InN(001) because of the similarity in atomic arrangement between the (1 1 1) plane of Si and the (0 0 1) plane of InN. In addition, the proportion of nanorods distributed in the range (0–2°) ascends with increase in nitriding time and the distribution range of deviation angle narrows down accordingly. The weighted mean ($\bar{X}$)and standard deviation value (S) of the θ are calculated to simply evaluate the orientation and distribution of InN nanorods. The weighted mean and standard deviation are calculated by the following equations:

$$\bar{X} = \sum fx/n \tag{1}$$

$$S = \sqrt{\sum f(x-\bar{X})^2/n-1} \tag{2}$$

where f = frequency; x = class mid-value; $n = \sum f$.

The calculated deviation angles of InN nanorods in samples (g), (h), and (i) are 5.44° ± 4.19°, 4.04° ± 3.62°, and 1.96° ± 2.63°, respectively. The weighted mean approaches 0° with longer nitriding time. In addition, the smaller the standard deviation is, the narrower the distribution range of deviation angle is. These facts suggest that the vertical orientation of InN nanorods can be enhanced by extending the nitriding time.

Fig. 5 demonstrates the XRD patterns of samples (a), (b), (c), (g), (h) and (i). The peaks at 2θ = 31.44°, 43.30°, 57.07°, 58.92°and 65.45° are assigned to the InN(0 0 2), InN(1 0 2), InN(1 0 3), Si(2 2 2) and InN(0 0 4) planes, respectively. It indicates that InN(0 0 2) and (1 0 2) peaks appeared when InN nanorods were grown on bare Si(1 1 1) substrate. When Si(1 1 1) substrate was nitrided for 1 min, the InN(1 0 3) peak appeared besides the