Short communication

In-assisted growth of InN nanocolumn on Si(111) substrate by molecular beam epitaxy

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ABSTRACT

We have demonstrated that the thickness of the catalyst layer plays a significant role in the morphology and the material quality of the InN nanocolumns grown on Si(111) substrate by plasma-assisted molecular beam expitaxy using vapor-liquid-solid method. A systematic investigation of In catalyst films was undertaken, revealing that high density uniform InN can not be obtained when the In catalyst is either too thin or too thick and the appropriate thickness of the deposited In was 1 nm. The influence of V/III radio on the growth procedure is also discussed, and as proved, a higher V/III radio is necessary to be used to get high density nanocolumns and improved optical property.

III-N semiconductors are useful for solid state lighting [1], high power electronics [2], ultraviolet emitters [3,4], solar energy conversion [5,6], and sensors [7]. Within the III-N family, InN stands out due to its narrow bandgap (0.65 eV) [8,9], very high electron mobility [10,11] and large saturation velocity, marking it a potential candidate for high-speed and high frequency electronic [12,13] and optoelectronic [14] devices.

The synthesis of InN film is hampered by the lack of a lattice-matched substrate and the thermal instability of InN [15—17], leading to highly defective films. In contrast, InN nanostructures can be grown with relatively high quality. Nanocolumns (NCs) favor highly effective lateral stress relaxation and thus exhibit drastically reduced defects in heterostructures. This is especially beneficial for large lattice-mismatched systems, such as InN, which is usually grown on foreign substrates. InN NCs have attracted much attention recently as they are not only suitable for studying fundamental properties, but also as building blocks for nanoscale devices, such as infrared emitters, biosensors, and solar cells [18—21]. The growth of nanocolumn has been explored by using various methods and mechanisms such as the vapor-phase transport process, chemical vapor deposition, pulsed laser deposition by using vapor-solid (VS) or vapor-liquid-solid (VLS) mechanism, and solution process [22—24]. Among them, the VLS mechanism is preferential for nanocolumn growth. This is because the nanocolumn growth proceeds from a liquid catalyst proceeds 10 to 100 times more rapidly than that from a solid buffer layer. Moreover, it is relatively easy to control the size of the nanocolumn diameter which has a direct impact on the electrical and optical properties of the nanocolumns because of the surface and confinement effect [25—27]. It is important to control the size of the nanocolumn diameter systematically for device application. As for VLS, the role of the catalyst is important for the growth of nanocolumns with controlled morphology and dimensions, and the size of the catalyst determines the diameter of the NCs.

In this work, we investigate the effects of the size of In catalyst and V/III radio on the material properties and the formation of InN nanocolumns grown on the Si (111) substrate by In-catalyzed VLS method. All the growth experiments were carried out by RF-MBE using metallic In and RF-activated nitrogen plasma as the sources. The In atomic beam was supplied by conventional Knudsen cell. Activated nitrogen was supplied from a commercial radio-frequency plasma source (Oxford Scientific) with a highly pure N_2 gas (6N). InN nanocolumns were characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD) and photo-luminescence (PL) spectroscopy.

Prior to growth, the substrate was ultrasonically cleaned in

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Table 1
Experimental details of the In film's deposition and of the VLS assisted growth of InN nanocolumns.

	No. of the experiment	In film thickness (nm)	T_{sub} (°C)	T_{In} (°C)	N_2 flux (sccm)	Plasma power (W)
Series A	A_1	1	475	655	0.35	400
	A_2	2	475	655	0.35	400
	A_3	3	475	655	0.35	400
	A_4	4	475	655	0.35	400
Series B	B_1	1	475	640	0.40	400
	B_2	0.5	475	640	0.40	400
	B_3	0.1	475	640	0.40	400
	B_4	0	475	640	0.40	400

acetone, ethanol and deionized water, each for 5 min. After that, the substrate was loaded into the growth chamber of our system to do the thermal desorption procedure at the pressure of 8.0×10^{-10} mbar.

The InN nanocolumns were deposited at the temperature of 475 °C in a RF-MBE System. Two series of samples were made. For Series A, In layers of various nominal thicknesses ranging from 1 to 4 nm were deposited. The In film was annealed at 500 °C for 5 min in order to make sure that the In film was fully transformed into the In droplets, and after turning down the temperature to 475 °C opened the cover of In and N source to start the growth procedure. The samples achieved were named A_1, A_2, A_3 and A_4. For Series B, we increased the V/III radio during the growth procedure in order to form the nanocolumn more effectively, and decreased the In layers thickness much further to explore the optimal value to get InN nanocolumn arrays. The samples in Series B were B_1, B_2, B_3 and B_4. Details about the experimental conditions are compiled in Table 1.

Fig. 1 shows SEM images of the four samples in Series A, which were grown on Si(111) substrates coated with 1 nm (a), 2 nm (b), 3 nm (c), 4 nm (d) In catalyst. As shown in Fig. 1(a), clusters in nanoscale were grown on the substrate and almost all the clusters in larger size are hexagonal structure which is in accordance with InN. However, the other three images (b), (c), and (d) are quite different from image (a). No nanoclusters or hexagonal InN but only punctiform morphology can be seen on the substrates. As shown in Fig. 1(e), the PL properties indicate that the near infrared photoluminescence peak of A_2 is quite weak than A_1, and what's more, there is no InN photoluminescence peak in A_3 and A_4. We consider that the dots may be In droplets in a large scale and no InN was composed during the growth procedure due to the excessively thick In film and the In-rich growth condition [28].

As previously shown, the morphology of the NCs in A_1 is not completely uniform. Thus, to optimize the growth procedure, the V/III ratio was adjusted to an appropriate value. Sample B_1, which the temperature of In source was changed from 655 °C to 640 °C, the N_2 flux was increased from 0.35sccm to 0.40sccm and its other growth parameters were as the same as Sample A_1, was made to compare with Sample A_1. Comparing with Sample A_1, the morphology of Sample B_1 was obviously improved which can be seen in Fig. 2(b). Their optical quality determined by photoluminescence (PL) spectroscopy was shown in Fig. 2(c). There were two major differences between A_1 and B_1. First, the PL peak was shifted to the lower energy when increasing the V/III ratio. In addition, the FWHM of PL band is 91 meV for B_1 and 99 meV for A_1. Both of the differences revealed the improvement of the InN quality. Thus, the optimized growth condition was adopted to get high density uniform InN nanocolumns in the subsequent samples. The In catalyst thickness continued to be reduced, and the samples prepared were named Sample B_2, B_3 and B_4 with 0.5 nm, 0.2 nm and 0 nm In catalyst thickness, respectively. Fig. 3(a)–(d) are the SEM images of InN nanocolumns grown on the Si(111) substrates in Series B. When the In catalyst thickness is 1 nm, as shown in the enlarged SEM images of Fig. 3(a), the epitaxial InN nanocolumns exhibit obviously higher density and smaller diameter in despite of the existence of large size nanocolumns. With the decreasing of In catalyst thickness, as seen in Fig. 3(b) and (c), the catalysis is greatly reduced which lead to the formation of larger size nanocolumns and a trend of mergence. As for the sample without In catalyst, it can be observed that the nanocolumns have coalesced into a compact film structure which can be seen in Fig. 3(d). Therefore, it is believed that an appropriate thickness of In catalyst and the V/III ratio is in favor of the formation of high density uniform InN nanocolumns.

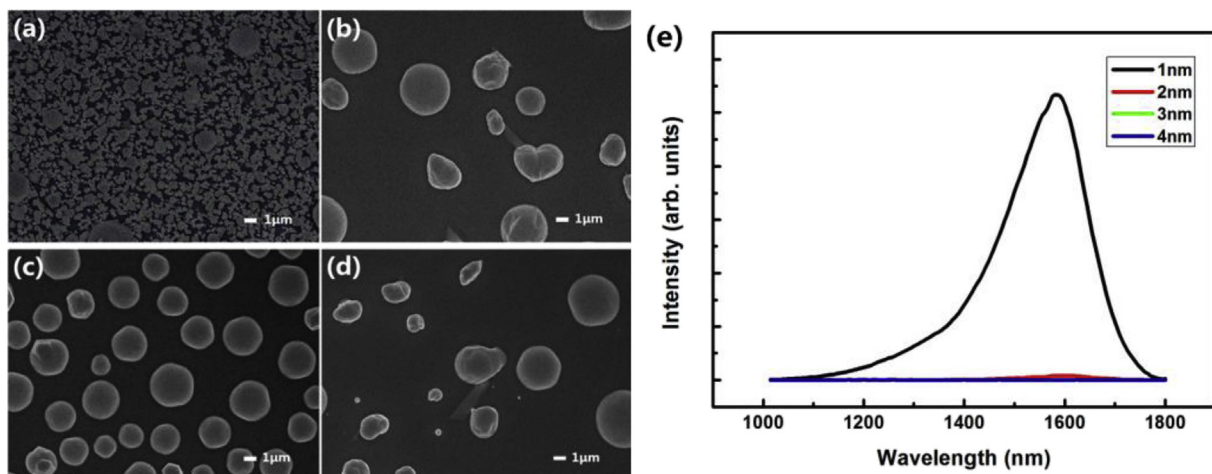The XRD patterns of all samples in Series B are displayed in

Fig. 1. SEM images of the four samples in Series A with 1 nm (a), 2 nm (b), 3 nm (c) and 4 nm (d) In catalyst films on Si(111) substrate. (e) Photoluminescence spectra of A_1, A_2, A_3, and A_4 at room temperature.