Growth mechanism, structure and IR photoluminescence studies of indium nitride nanorods

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Abstract

High-quality single crystal indium nitride nanorods were grown on Si substrates by catalytic chemical vapor deposition. Both Raman and high resolution transmission electron microscopic analyses suggested that even a minute amount of oxygen, from the residual oxygen in the growth environment and/or native oxide on the Si, would effectively help the growth of InN nanorods. The In₂O₃ formed on Au nanoparticles helped dissolve nitrogen as a catalyst with the subsequent growth of InN nanorods. Variations in the apparent color and photoluminescence (PL) spectra of the InN nanorods were observed. For the optically brown InN nanorods that exhibited diameters in the range of 30–50 nm, the PL study showed a peak at 1.9 eV, the possible origins of which are discussed. In contrast, for the optically black InN nanorods that exhibited diameters in the range of 50–100 nm, the PL peak at approximately 0.766 eV measured at 20 K was attributed to band edge emission.

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1. Introduction

One dimensional (1D) nanomaterials such as nanowires and nanorods could possess some distinctive properties that might be fundamentally different from their bulk or thin film counterparts,

therefore, they have the potential for advanced applications [1]. Various strategies have been successfully developed for the fabrication of 1D semiconductors. By the collective efforts of many researchers, the growth mechanisms used can now be classified into the vapor–liquid–solid (VLS), vapor–solid (VS) and template confinement methods [2]. A comprehensive compilation of the syntheses and characterization of nanowires and nanorods for the technologically important group

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III (Al, Ga, and In)-nitrides has just been published recently [3], and a few reports on GaN nanowires have also shown some interesting structural and optoelectronic characteristics [4,5]. In comparison to the extensively researched GaN, studies on InN are still scant. In fact, overall InN has not received as much attention as that given to GaN. This is probably due to the difficulties in growing high-quality crystalline InN samples, not only nanowires and nanorods, but even thin films. The controversy about its fundamental band gap [6,7] can be partly explained by the various forms of defects present in InN films. It is thus of significance that free-standing high-quality nanowires and nanorods can be synthesized, since they may be useful in understanding the fundamental properties of InN.

We have previously reported on the growth and characterization of InN nanorods by a simple catalytic chemical vapor deposition technique [8], wherein Au is used as the primary catalyst for growing InN nanorods. However, details of the growth mechanism were not very clear. In particular, we found that oxygen incorporation during growth is indispensable for producing high-quality and large-quantities of InN nanorods. It should be emphasized that our case is different from the so-called oxide-assisted 1D growth, as reported originally for the synthesis of large quantities of Si, Ge, GaAs and GaN nanowires [3,9] in that a larger quantity of oxide was employed and even incorporated in their case. For instance, mixed GaAs and Ga_2O_3 powders were used as targets in a laser ablation system to grow GaAs nanowires covered by an amorphous GaO_x sheath [9]. In contrast, only very minute amount of oxygen is allowed in the growth of InN nanorods. Introducing excessive oxygen would lead to the formation of In_2O_3 , instead of InN nanorods.

In order to investigate the growth mechanisms for InN nanorods, the structural properties for different growth times were carefully analyzed in this work. Both Raman and transmission electron microscopy techniques were employed for this purpose. It is suggested that the Au thin films transform to Au/InO_x nanoclusters during the early stages and serve as a catalyst for the

subsequent growth of InN nanorods. Furthermore, except at the very end of the individual InN nanorods where the Au/InO_x nanoclusters resided, the rest of the rod was single-crystal InN of high quality with no detectable Au or oxygen. Finally, photoluminescence (PL) properties of these well-separated and nearly defect-free InN nanorods were found to be strongly dependent on the diameter of the nanorods, the implications of which will be discussed.

2. Experimental procedure

Ultrasonically cleaned Si (1 0 0) wafers with and without hydrofluoric acid etching were used as substrates for InN nanorod deposition. The Si substrates were first coated with a 3-nm-thick Au film by ion beam sputtering under 5×10^{-4} Torr. Pure indium powders (ACROS, 99.999%) were placed in an alumina boat and served as the indium vapor source upon heating. The gold-coated silicon substrate was put face-down on the top of the alumina boat and then loaded into the central zone of a one-inch quartz tube, which was housed in a conventional tube furnace. This quartz tube was degassed to 10^{-1} Torr by a mechanical pump and then purged with ammonia (NH_3) with a flow rate of 50 sccm as the atomic nitrogen source. Standard growth procedures for InN nanorods are described as following. The temperature of the furnace was increased at a rate of $50^\circ\text{C}/\text{min}$ to 500°C at a pressure of 1 atm and held there for 3 h and then decreased at the same rate to room temperature. Morphologies and the crystal structure of the resulting materials on the Si substrate were characterized using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and X-ray powder diffraction (XRD, Toshiba, A-40-Cu) techniques. Further structural analysis of individual InN nanorods was performed using high-resolution transmission electron microscopy (HRTEM, JEOL JEM-4000EX) and selected-area electron diffraction (SAED) techniques. The HRTEM samples were prepared by dropping a droplet comprised of methanol and InN nanorods onto a Cu grid covered with a holey carbon film. Raman

scattering was measured at room temperature by means of a Renishaw 2000 micro-Raman spectrometer in the backscattering geometry using a 532.2 nm Nd-YAG laser as the excitation source. For PL measurements in the infrared (IR), an InGaAs detector was used and a 100 mW Ar^+ 488 nm laser was employed as the excitation source.

3. Results and discussions

Fig. 1 shows two typical FESEM images of the nanorods grown on the 3-nm-thick Au thin film covering the Si (100) substrate. Basically, all of

Fig. 1. Field emission scanning electron microscope images of catalytic-CVD grown InN nanorods that appear in the (a) brown and (b) black regions.

these InN samples exhibited two colors as observed by the naked eye in different regions of the substrate. The micrograph of the brown region near the edge of the substrate is shown in Fig. 1a, and that of the black region at the center of the substrate is shown in Fig. 1b. The diameter of the black nanorods is in the range of 50–100 nm while that of the brown ones is in the range of 30–50 nm. Note that the same growth conditions produced both the optically brown and black InN nanorods but on different regions of the substrate. The region of the substrate in the upstream portion of the NH_3 flow produced the optically brown InN nanorods whereas those placed further downstream produced predominantly black nanorods. However, the InN nanorods cease to form on the substrate when placed too far downstream in the NH_3 flow. A temperature variation of the NH_3 gas is expected since the period of time in the hot zone increases as it travels along the length of the quartz tube. This indicates that a temperature graded dissociation of NH_3 may be responsible for the observed brown and black nanorods. The apparent color difference implies structure-sensitive optical properties that will be discussed later.

Fig. 2a displays the X-ray diffraction (XRD) spectrum of InN nanorods. Besides signals from wurtzite InN (JCPDS 02-1450), cubic In_2O_3 (JCPDS 06-0416) signals having relatively weaker intensities can also be found. Raman spectra, measured at room temperature (RT), for InN nanorods from both brown and black regions are shown in Fig. 2b. Besides the Raman peak of Si at 520 cm^{-1} , the Raman-active phonon bands of InN at around 455, 489 and 569 (or 585 for black region) cm^{-1} corresponding to the $\text{A}_1(\text{TO})$, E_2 and $\text{A}_1(\text{LO})$ modes, respectively, were observed. Compared to the values reported for epi-quality InN thin films, there is a clear shift of the $\text{A}_1(\text{LO})$ peak towards lower wave numbers for InN nanorods collected from the brown region and barely no shift of $\text{A}_1(\text{LO})$ for those from the black region. This can be attributed mainly to the size confinement effect [8,10].

HRTEM studies indicated that every individual InN nanorod was capped with an In_2O_3 encapsulated Au catalyst. Fig. 3 displays the HRTEM images taken from three different regions of the

(a)

(b)

Fig. 2. (a) Broad-area XRD spectrum of the InN nanorods. (b) Typical Raman spectra of InN nanorods that appear in the brown and black regions.

nanorod, namely, the very end, the catalyst and the main body. The outer shell of the catalyst displayed in Fig. 3a clearly shows a lattice plane of In_2O_3 (110) with a d-spacing of 0.715 nm as indicated by the arrows. Fig. 3b shows an HRTEM image of the encapsulated catalyst and corresponding SAED pattern (inset). Three phases are observed in Fig. 3b and they can be assigned to In_2O_3 , Au and InN. The major diffraction pattern in the inset is indexed as the cubic In_2O_3 (c- In_2O_3) along the [1 1 1] direction. In the same pattern, the weak diffraction spots (black open circles) are identified as hexagonal InN (h-InN) with zone axis of [0 0 1]. Meanwhile, since the c- In_2O_3 (440) and the h-InN (110) have almost the same d-spacing and both c- In_2O_3 [1 1 1] and h-InN [0 0 1] axes have

Fig. 3. (a) HRTEM of In_2O_3 in the outer shell of the Au catalyst. (b) HRTEM image of the encapsulated catalyst of a single InN nanorod shows the relative positions of Au, In_2O_3 and InN. The corresponding SAED pattern is shown in the inset. (c) HRTEM and the corresponding SAED pattern (inset) of the main body of an InN nanorod.

the same 3-fold symmetry, the diffraction spots marked with black open squares could be the overlap patterns of c- In_2O_3 and h-InN. Moreover,

the gold pattern (white circles) is also found and the composition is further confirmed by using energy dispersive X-ray measurements with the TEM. Fig. 3c gives a HRTEM micrograph and the corresponding SAED pattern (inset) of the main body of the InN nanorod. The wurtzite structure of InN with [001] zone axis and the [110] growth direction are identified. Here, it should be mentioned that these InN nanorods have no outer sheath in contrast to those synthesized by the oxide-assisted growth method.

The encapsulation of Au by In_2O_3 is somewhat unexpected from a conventional understanding of the VLS growth, as one would expect a direct connection of Au with InN nanorods. On the other hand, an epitaxial relationship between InN and In_2O_3 is always found in our TEM observation, due to their close proximity in lattice spacing and symmetry. Along the InN [110] growth direction and the In_2O_3 [440] direction with the same two-fold symmetry, the InN (002) and the In_2O_3 (0–20) are related almost exactly by a factor of 9:5 with a lattice mismatch of less than 1.3% at RT. In addition, the InN (1–10) and In_2O_3 (440) are related almost exactly by a factor of 3:9 with a lattice mismatch of less than 3.2% at RT.

In order to further study the growth mechanism of InN nanorods, we carried out a series of experiments, keeping the growth conditions the same while we monitored the structural evolution as a function of the growth period at 500°C increased from 0 to 180 min. The Raman spectra taken from samples grown with different holding times are shown in Fig. 4. Firstly, for sample prepared with a holding time of 0 min, which means rapid cooling after reaching 500°C, the Raman peaks at 306 and 623 cm^{-1} [11] can be attributed to those of indium oxide and no other Raman peak appears except for the 520 cm^{-1} peak from the Si substrate. When the holding time was gradually increased, the Raman peaks of InN started to appear and their intensity also became more and more pronounced while those of indium oxide started to diminish. For the sample prepared with a holding time of 180 min, only the Raman peaks of InN were observed and there were hardly any detectable indium oxide signals. This therefore indicates that the oxide, which is relatively small

Fig. 4. Raman spectra of the samples grown at 500°C with a holding time of (a) 0 min, (b) 30 min, (c) 90 min, and (d) 180 min, respectively.

and only appears in the early growth stage, may be derived from the residual oxygen in the chamber or native oxide on the Si substrate. However, the InN nanorods grown on HF etched and unetched Si substrates showed no difference in the In_2O_3 signals, coming from the In_2O_3 sheathed Au nanoparticles, prompting us to believe that the dominant contribution was from the residual oxygen in the chamber. This is possible since the chamber (quartz tube) was degassed to only 10^{-1} Torr using a mechanical pump. Furthermore, because the ammonia gas would decompose to form NH, NH_2 , H_2 , and N_2 at high temperature, this oxygen would be released very quickly at the subsequent growth stage. According to these observations, indium oxide seems to be crucial for the growth of InN nanorods.

The co-existence of indium oxide and Au in the cap of InN nanorods is quite intriguing. To resolve the different functions of indium oxide and Au, we have experimented using indium oxide nanoparticles alone without any Au on Si to grow InN nanorods. We found that InN nanorods would also form directly on indium oxide nanoparticles but the yield is much lower than that produced by using Au as a catalyst. Meanwhile, if we applied Au as a catalyst onto a pre-patterned Si substrate wherein some areas had a thicker oxidized layer while others were free of oxygen, we found that

InN nanorods would grow preferentially within the Au/SiO_x/Si areas. This implies that the effective growth of InN nanorods can not be achieved unless both indium oxide and gold coexist as the catalyst.

Based on the above results, the growth mechanism of InN nanorods is proposed to be as follows. Fig. 5 illustrates a schematic diagram of this growth model. First, ultra-fine Au–In liquid alloy droplets will be formed below 500°C (Fig. 5a). However, due to the presence of a minute amount of residual oxygen or the native oxide on silicon, InO_x, which is energetically more favorable than InN to form, covers the surface of Au–In alloy droplets, resulting in core-shell Au@InO_x nanoclusters (Fig. 5b) [12]. Literature data of the Gibbs free energies (*G*) for the formation of InN and In₂O₃, under conditions close to ours, are listed as follows [13]:

It is quite clear that the formation of In₂O₃ would be much more favorable, because of its larger negative value in *G*, and In₂O₃ would continue to grow until the oxygen is completely

Fig. 5. Schematic diagram of the growth mechanism for InN nanorods. (a) Au nanoclusters are formed at first. (b) Oxygen and In vapors dissolve in Au nanoclusters to form Au/InO_x nanoclusters in the early growth stage. (c) In vapor and N from the decomposition of NH₃ are absorbed in InO_x inducing the growth of InN nanorod. (d) The In₂O₃ encapsulated Au catalyst resides at the cap of InN nanorod after cooling.

consumed. When the temperature is increased to 500°C, it is speculated that N from the ammonia source would then dissolve in the Au@InO_x nanoclusters (Fig. 5c) presumably with the formation of In–O–N as an intermediate state, due to the low miscibility of N and Au, before further reaction of N with In to form the InN nanorods (Fig. 5d).

Fig. 6 shows the PL spectra at 20–140 K from the black InN nanorods grown on the Si substrates. A strong band edge PL emission at 0.766 eV was observed at 20 K. The PL peak energy shifted slightly from 0.766 to 0.762 eV with an increase in the measurement temperatures from 20 to 140 K. This is very different from Wu's result for InN thin films that shows a blue shift with increasing temperature [7]. The IR PL intensity of our black InN nanorods dramatically decreased with an increase in the measurement temperature, and there was no detectable IR PL emission at temperatures higher than 150 K. In contrast, InN nanorods in the brown region lacked the IR PL emission, but had a strong and broad emission band near 1.9 eV even at room temperature (inset, Fig. 6) [8]. This emission (micro PL) was measured using the Renishaw 2000 micro Raman

Fig. 6. Temperature dependent PL spectra of the black InN nanorods measured at (a) 20 K, (b) 60 K, (c) 100 K and (d) 140 K. The dashed line labels the peak position of 0.766 eV obtained at 20 K. The inset shows the PL spectrum from the optically brown InN nanorods measured at RT using the micro PL setup (Renishaw 2000).

spectrometer. The origin of the visible PL around 1.9–2.1 eV is discussed below.

The variation of the PL peak position for InN nanorods, from the IR to the visible, could be attributed to several possible reasons. The first one is different oxygen content in the two kinds of InN nanorods in different regions. Effects of oxygen incorporation in InN on its optical properties have been reported by Yoshimoto et al. [14]. However, there is no direct evidence in our case that nanorods in the brown region would have more oxygen content than those in the black region causing the emission peak shift from 0.766 to 1.9 eV. Furthermore, ascribing the 1.9 eV peak solely to the In_2O_3 phase is not persuading since this peak was not prominent in the black region although all the InN nanorods were capped with In_2O_3 encapsulated Au catalysts. The second possibility may be the so-called quantum size effect. In particular, the effective mass of InN has recently been reported to be as low as 0.042 m_0 , hence a strong quantum size effect is expected [15]. To shift the fundamental energy band gap of InN from 0.766 to 1.8–2.1 eV, the crystal size (or well-ordered domain) of InN is estimated to be about 5 nm. However, the diameter of our brown InN nanorods is in the range of 30–50 nm. Therefore, the quantum size effect could not adequately explain the unusually large shift either. On the other hand, the Burstein-Moss shift, occurring at a high carrier concentration with the conduction band (for an n-type semiconductor) being significantly filled due to the limited density of states, can result in a large shift of the absorption edge energy and PL, and has been demonstrated in nearly oxygen-free InN films by Wu et al. and Davydov et al. [16,17]. However the reported shift, of about 0.5 eV as the free electron concentration was increased by over two orders in magnitude [16], falls short of the shift (~ 1.1 eV) observed here. The Burstein-Moss shift could also occur in our case, as a result of unintentional doping, but further experiments are needed to demonstrate it. Nevertheless, the fact that the IR PL peak was only observed for the nearly defect-free black InN nanorods with relatively large diameter (50–100 nm) and the increase in PL peak position with decreasing size

seems to support a fundamental band gap of InN in the IR region.

4. Conclusion

In summary, the growth mechanism of InN nanorods has been studied by carefully analyzing the products in the early growth stages. Formation of indium oxide during early growth stage, as supported by Raman studies, played a crucial role in producing large-quantities of high-quality InN nanorods. TEM investigations revealed that the InN nanorods were capped with an In_2O_3 encapsulated Au catalyst and some epitaxial relation between the single crystal InN nanorod and the In_2O_3 cap was observed. Furthermore, InN nanorods having larger diameters (> 50 nm) appeared black while those of smaller diameters appeared brown. For the brown InN nanorods, a pronounced visible PL peak has been observed at room temperature, the origins of which are yet to be clarified. Low temperature PL measurements of the black InN nanorods showed an emission peak near 0.766 eV, which is ascribed to band-edge emission.

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