An investigation into the conversion of In$_2$O$_3$ into InN nanowires

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Abstract
Straight In$_2$O$_3$ nanowires (NWs) with diameters of 50 nm and lengths $\geq 2$ $\mu$m have been grown on Si(001) via the wet oxidation of In at 850°C using Au as a catalyst. These exhibited clear peaks in the X-ray diffraction corresponding to the body centred cubic crystal structure of In$_2$O$_3$ while the photoluminescence (PL) spectrum at 300 K consisted of two broad peaks, centred around 400 and 550 nm. The post-growth nitridation of In$_2$O$_3$ NWs was systematically investigated by varying the nitridation temperature between 500 and 900°C, flow of NH$_3$ and nitridation times between 1 and 6 h. The NWs are eliminated above 600°C while long nitridation times at 500 and 600°C did not result into the efficient conversion of In$_2$O$_3$ to InN. We find that the nitridation of In$_2$O$_3$ is effective by using NH$_3$ and H$_2$ or a two-step temperature nitridation process using just NH$_3$ and slower ramp rates. We discuss the nitridation mechanism and its effect on the PL.

Introduction
Group III-Nitride (III-N) semiconductors have been investigated extensively over the past decades due to their applications as electronic and optoelectronic devices. In addition, they are promising for the realization of high efficiency, multi-junction solar cells since their band-gaps vary from 0.7 eV in InN through to 3.4 eV in GaN up to 6.2 eV in AlN; thereby, allowing the band gaps of the ternaries In$_x$Ga$_{1-x}$N and Al$_x$Ga$_{1-x}$N to be tailored in between by varying $x$. Nanowires solar cells (NWSCs) are also receiving increasing attention so far they have been fabricated from Si and metal-oxide (MO) NWs. Nitride NWs such as InN [1], GaN [2] and AlN [3] are, therefore, promising for the realization of full-spectrum third generation NWSCs. However, their growth and properties must be understood beforehand in order to make nanoscale devices. So far we have grown InN [1] and GaN NWs [2] using the direct reaction of In or Ga with NH$_3$, while more recently we showed that Ga$_2$O$_3$ NWs may be converted to GaN by post-growth nitridation using NH$_3$ and H$_2$ [4]. Here, we have undertaken a systematic investigation into the conversion of In$_2$O$_3$ to InN NWs, which has not been carried out previously by others, thereby complementing our earlier work on the conversion of Ga$_2$O$_3$ to GaN NWs.

Therefore, we have grown straight In$_2$O$_3$ NWs with diameters of 50 nm and a high yield and uniformity. We find that the post-growth nitridation of In$_2$O$_3$ NWs using NH$_3$ leads to the elimination of the NWs above 600°C. The In$_2$O$_3$ NWs are preserved for temperatures less than 700°C but are not converted into InN even after long nitridation times of 6 h. However, the nitridation process was enhanced significantly via the use of H$_2$ or by employing a two-step temperature nitridation process, which also lead to a suppression of the photoluminescence (PL) peak at 550 nm similar to the nitridation of Ga$_2$O$_3$ NWs [4].

Experimental method
Initially In$_2$O$_3$ NWs were grown using an atmospheric pressure chemical vapour deposition (APCVD) reactor described elsewhere [5]. For the growth of In$_2$O$_3$ NWs, 0.2 g of fine In powder (Aldrich, Cyprus, Mesh 100, 99.99%) was weighed and loaded in a quartz boat, while square pieces of $n^+$ Si(001) $\approx$ 7 mm $\times$ 7 mm, coated with $\approx$1.0 nm of Au, were loaded at various distances from the In. The Au layer was deposited via sputtering using Ar under a pressure of $\approx$10$^{-3}$ mBar. The boat was positioned directly above the thermocouple used to measure the heater temperature at the centre of the 1"
quartz tube (QT). Another quartz boat with ≈5 ml of de-ionised (DI) H2O was positioned at the inlet of the tube. After loading the boats at room temperature (RT), Ar (99.999%) was introduced at a flow rate of 500 standard cubic centimetres per minute (sccm) for 10 min. Following this, the temperature was ramped to 850°C under a flow of 50 sccm Ar using a ramp rate of 30°C/min. Upon reaching the growth temperature (Tem), the flow of Ar was maintained at 50 sccm for 30 min in order to grow the In2O3 NWs after which the reactor was allowed to cool down in a flow of 50 sccm of Ar for at least 30 min. The sample was always removed only when the temperature was lower than 100°C.

The nitridation of the In2O3 NWs was carried out in a new 1" QT without any solid precursors. After loading each sample with In2O3 NWs from the downstream side, a flow of 500 sccm Ar was introduced for 10 min after which the temperature was ramped to the nitridation temperature (Tn) under a flow of NH3 that varied between 125 and 250 sccm using a ramp rate of 30°C/min. Upon reaching Tn, the same flow of NH3 was maintained for various times between 1 and 6 h after which the reactor was allowed to cool down to RT under the same flow of NH3. A list of the different temperatures, nitridation times and NH3 gas flows used for the nitridation of the In2O3 NWs are shown in Table 1. Similarly nitridation was carried out using NH3 and H2. In this case, the temperature was ramped to 500°C under a flow of NH3 and H2 whose relative flows varied using a ramp rate of 10°C/min. Upon reaching Tn, the same flow of NH3 and H2 was maintained for 1 h. Then, the temperature was ramped to 700°C and the same flow of NH3 was maintained for 30 min after which the reactor was allowed to cool down to RT.

The morphology of the as grown In2O3 NWs and those treated with NH3 were examined with a TESCAN scanning electron microscope (SEM), while their crystal structure and phase purity were investigated using a SHIMADZU, X-ray diffraction (XRD-6000), with Cu-Ka source, by performing a scan of θ - 2θ in the range between 10° and 80°. Finally, PL measurements were carried using above bandgap (approx. 3.75 eV [6]) excitation at 267 nm. The pulse excitation was the second harmonic of a beam from an optical parametric amplifier pumped with a mode-locked TiSapphire laser. The pulses were 100 fs FWHM at a repetition rate of 250 kHz. The energy per pulse incident on the samples was 40 pJ over a spot of 2 mm in diameter.

**Results and discussion**

Previously, we obtained In2O3 NWs by dry oxidation at 700°C [7]. A high yield of In2O3 NWs with an average diameter of ≈100 nm and lengths of ≈1 μm was obtained on Si(111) and quartz. However, these In2O3 NWs were slightly tapered; their diameters were larger and lengths were shorter compared to the In2O3 NWs obtained here by wet oxidation. Moreover, the distribution of the In2O3 NWs obtained by wet oxidation was far superior and much more uniform compared to those obtained by dry oxidation. A typical image of In2O3 NWs that were obtained at Tg = 850°C by wet oxidation is shown in Figure 1. It should be pointed out that a high yield and uniform distribution of In2O3 NWs extending over 1 cm2 was obtained when the distance between the In and the Au/n+Si (001) was ≥15 mm, which led to a light blue-like deposit. The In2O3 NWs

| Table 1 Summary of post-growth nitridation conditions for the conversion of In2O3 NWs to InN |
|----------------------------------------|----------------------------------------|----------------------------------------|
| **(I) Tn (°C)**                       | **(II) t (h)**                         | **(III) %H2**                          |
| CVD797 500°C                         | CVD850 500°C 3 h                      | CVD855 10                               |
| CVD788 600°C                         | CVD853 500°C 6 h                      | CVD856 20                               |
| CVD790 800°C                         | CVD795 600°C 1 h                      | CVD857 40                               |
| CVD791 900°C                         | CVD849 600°C 2 h                      | CVD859 80                               |
|                                      | CVD848 600°C 3 h                      |                                        |

Initially a flow of 500 sccm of Ar was introduced into the reactor after which the temperature was ramped to Tn at 30°C/min under a flow of (I) 250 sccm of NH3, (II) 125 sccm of NH3 and (III) under different flows of NH3 and H2, but keeping the total flow constant at 200 sccm. Upon reaching Tn, the same flows were maintained for 1 h at various temperatures (I), different nitridation times at 500 and 600°C (II) and for 1 h at 500°C (III).
have diameters of \( \approx 50 \) nm, lengths \( \geq 2 \) \( \mu \)m and exhibited clear peaks in the XRD as shown in Figure 2 by the top curve, corresponding to the body centred cubic (bcc) crystal structure of In\(_2\)O\(_3\) with \( a = 10.12 \) Å, in agreement with Dai et al. who obtained twisted In\(_2\)O\(_3\) NWs by wet oxidation [8]. The In\(_2\)O\(_3\) NWs shown in Figure 1 are straight [9,10] and in our case In\(_2\)O\(_3\) NWs grow by a simple chemical route involving the following reaction: \( 2\text{In} + 3\text{H}_2\text{O} \rightarrow \text{In}_2\text{O}_3 + 3\text{H}_2 \) [8]. Wet oxidation is a facile method and generally occurs faster than dry oxidation. No NWs were obtained on plain Si(001), suggesting the growth of In\(_2\)O\(_3\) NWs occurs via the vapour-liquid-solid (VLS) mechanism with Au acting as the catalyst. In this case, Au NPs absorb In until they become supersaturated after which In\(_2\)O\(_3\) NW growth commences via the reaction of In with H\(_2\)O as outlined above.

The PL spectrum following excitation at 267 nm at 300 K consisted of two broad peaks, centred at 400 and 550 nm as shown in Figure 3. Similar peaks in the PL have been observed by Yan et al. [11] who obtained a broad luminescence band centred at 395 nm from In\(_2\)O\(_3\) nanorods, Liang et al. [12] who found a peak at 470 nm from In\(_2\)O\(_3\) nanofibres and Wu et al. [13] who observed two distinct peaks at 416 and 435 nm from In\(_2\)O\(_3\) nanowires. It is important to point out that these peaks are commonly attributed to the presence of oxygen vacancies.

Next, we will describe the conversion of In\(_2\)O\(_3\) NWs into InN and in particular consider the nitridation of In\(_2\)O\(_3\) NWs at different temperatures. To begin with In\(_2\)O\(_3\) NWs were subjected to 250 sccm of NH\(_3\) for 1 h at various temperatures between 500 and 900°C as listed in Table 1.

The XRD spectra of the In\(_2\)O\(_3\) NWs treated at different temperatures is shown in Figure 2. As can be seen most of the oxide peaks disappear at temperatures \( >600°C \) above 600°C, a new peak appears, which corresponds to the (101) crystallographic direction of InN [1]. Furthermore, SEM images reveal that the In\(_2\)O\(_3\) NWs have been eliminated above 600°C, but a thin layer of InN remains on the Si(001). Evidently, the nitridation of the In\(_2\)O\(_3\) NWs is destructive above 600°C due to the fast decomposition of In\(_2\)O\(_3\) to In\(_2\)O, which is a gas. We should also point out that in addition to the temperature we also varied the nitridation time. In particular, we carried out nitridations of In\(_2\)O\(_3\) NWs at 500 and 600°C under a flow of 125 sccm NH\(_3\) for different times as described in Table 1.

Again the conversion of In\(_2\)O\(_3\) NWs to InN appears to be incomplete as can be clearly seen from the XRD spectra in Figure 4 where one can observe the presence of In\(_2\)O\(_3\) peaks and just one peak at (101) corresponding to InN. In order to achieve the efficient conversion of In\(_2\)O\(_3\) NWs to InN without eliminating them, we used two different approaches. In the first one, we have carried out post-growth nitridation, which included H\(_2\) as shown in Table 1 and in the second approach, we have utilised a two-step temperature nitridation process. The corresponding XRD spectra are shown in Figure 5. As can be seen from the XRD spectra, H\(_2\) plays a significant role in the removal of the oxygen and thus all major oxide peaks are eliminated and the conversion to InN is achieved with 40% H\(_2\). As already described above, NH\(_3\) alone does not promote the efficient conversion of In\(_2\)O\(_3\) NWs into InN at temperatures between 500 and
600°C. This is likely due to the formation of an InN shell around the In$_2$O$_3$ core, which prevents the diffusion of N into the In$_2$O$_3$ core. However, H$_2$ appears to promote the conversion of In$_2$O$_3$ into InN [14].

In addition, the two-step process lead to the effective conversion of In$_2$O$_3$ NWs to InN using just NH$_3$. In this case, the temperature was ramped at 10°C/min up to 500°C and held constant over a period of 1 h, after which the temperature was ramped again slowly to 700°C in order to promote the nitridation. Recall that the In$_2$O$_3$ NWs were eliminated during a single-step nitridation process at 700°C using a fast ramp rate of 30°C/min. However, it should be noted that the NWs treated by this two-step temperature nitridation process were bent probably due to the fact that the crystal structure changes from bcc to the hexagonal wurtzite structure, and there is a non-uniform strain distribution between the core and shell. The effect of the post-growth nitridations on the PL of the In$_2$O$_3$ NWs is shown in Figure 3.

In the case of the nitridation using just NH$_3$ for 3 h at 500°C, one may observe that there is no substantial change in the shape of the PL of the In$_2$O$_3$ NWs except from the fact that the PL intensity has been reduced. However, the nitridation of the In$_2$O$_3$ NWs using NH$_3$ and H$_2$ leads to a clear suppression of the peak at 550 nm, which is attributed to oxygen consistent with previous investigations on Ga$_2$O$_3$ [4]. The peak around 400 nm maybe attributed to In vacancies [15], but not O$_2$ as commonly suggested [11-13]. However, further work is required to clarify the origin of the PL peak around 400 nm.

Conclusions

Straight In$_2$O$_3$ NWs with diameters of 50 nm, lengths ≥2 μm and a bcc crystal structure have been grown on Au/Si(001) via the wet oxidation of In at 850°C. These exhibited two broad peaks in the PL, centred around 400 and 550 nm. The post-growth nitridation of In$_2$O$_3$ NWs was found to be effective by using NH$_3$ and H$_2$ at 500 and 600°C or a two-step temperature, nitridation process at 500 and 700°C. This lead to a suppression of the PL peak around 550 nm related to O$_2$ consistent with previous investigations on Ga$_2$O$_3$. In contrast, single-step temperature, nitridations using just NH$_3$, carried out with fast ramp rates above 600°C lead to the complete elimination of the In$_2$O$_3$ NWs, while they were not effective at 500 and 600°C.

Abbreviations

APCVD: atmospheric pressure chemical vapour deposition; bcc: body centred cubic; DI: de-ionised; MO: metal-oxide; NWs: nanowires; NWSCs: nanowires solar cells; PL: photoluminescence; QT: quartz tube; RT: room temperature; SEM: scanning electron microscope; VLS: vapour-liquid-solid; XRD: X-ray diffraction.

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Authors’ contributions section

MZ and PP carried out the growth, scanning electron microscopy and x-ray diffraction measurements. AO carried optical characterization. All authors read and approved the final manuscript.
Competing interests
The authors declare that they have no competing interests.

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References
1. Othonos A, Zervos M, Pervolaraki M: Ultrafast Carrier Relaxation in InN Nanowires Grown by Reactive Vapor Transport. Nanoscale Res Lett 2009, 4:122.
2. Tsokkou D, Othonos A, Zervos M: Defect states of chemical vapor deposition grown GaN nanowires: Effects and mechanisms in the relaxation of carriers. J Appl Phys 2009, 106:05431.
3. Li J, Nam KH, Nakarni ML, Lin JY, Jiang HX, Pierre Carrier, Su-Huai Wei: Band structure and fundamental optical transitions in wurtzite AlN. Appl Phys Lett 2003, 83:5163.
4. Othonos A, Zervos M, Christofides C: A systematic investigation into the conversion of β-Ga2O3 to GaN nanowires using NH3 and H2: Effects on the photoluminescence properties. J Appl Phys 2010, 108:124319.
5. Zervos M, Othonos A: Synthesis of Tin Nitride SnxNy Nanowires by Chemical Vapour Deposition. Nanoscale Res Lett 2009, 4:1103.
6. Aron Walsh, Da Silva Juarez LF, Su-Huai Wei, Körber C, Klein A, Piper LFJ, Alex DeMasi, Smith Kevin E, Panaccione G, Torelli P, Payne DJ, Bourlange A, Egdell R: Nature of the Band Gap of In2O3 Revealed by First-Principles Calculations and X-Ray Spectroscopy. Phys Rev Lett 2008, 100:167402.
7. Tsokkou D, Othonos A, Zervos M: Ultrafast time-resolved spectroscopy of In2O3 nanowires. J Appl Phys 2009, 106:084307.
8. Dai L, Chen XL, Jin JK, He M, Zhou T, Hu BQ: Fabrication and characterization of In2O3 Nanowires. Appl Phys A 2002, 75:687.
9. Qasemi A, EH-Maghraby EM, Yamazaki T, Kikuta T: Catalyst supported growth of In2O3 nanostructures and their hydrogen gas sensing properties. Sensors and Actuation B 2010, 147:48.
10. Calestani D, Zha M, Zappettini A, Lazzarini L, Zanotti L: In-catalyzed growth of high-purity indium oxide nanowires. Chem Phys Lett 2007, 445:251.
11. Yan Y, Zhou L: Competitive growth of In2O3 nanorods with rectangular cross sections. Appl Phys A 2008, 92:401.
12. Liang C, Neng G, Lee Y, Phillips F, Zhang L: Catalytic Growth of Semiconducting In2O3 Nanofibers. Adv Mater 2001, 13:1330.
13. Wu XJ, Hong JM, Han ZJ, Tao YR: Fabrication and photoluminescence characteristics of single crystalline In2O3 nanowires. Chem Phys Lett 2003, 373:28.
14. Guo L, Zhang Q, Li J: Preparation of ultrafine InN powder by the nitridation of In2O3 or In(OH)3 and its thermal stability. J Mater Chem 2003, 13:54.
15. Zhang J, Xu B, Jiang F, Yang Y, Li J: Fabrication of ordered InN nanowire arrays and their photoluminescence properties. Phys Lett A 2005, 337:121.

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