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MOLECULAR BEAM EPITAXY GROWTH OF HIGH-QUALITY InN NANORODS ON Si (111) SUBSTRATE

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ABSTRACT

The growth of high-quality InN nanorods (NRs) on Si (111) by plasma-assisted molecular beam epitaxy (PAMBE) is reported. X-ray diffraction and Raman spectroscopy investigations indicates that the NRs are wurtzite, c-axis oriented and single crystalline. Low temperature photoluminescence emissions with peak energy of ~ 0.75eV was observed indicating the high quality of the nanostructures. This study unravels a novel strategy for the successful growth of high-quality InN NRs on Silicon which is highly promising for applications in next generation nanodevices.

Keywords: InN Nanorods, Si(111), Improved quality, XRD, Raman Spectroscopy

INTRODUCTION

Indium Nitride (InN) materials have attracted increasing interest in the last few years due to their unique properties including light effective mass, high carrier mobility (Chang et al., 2009), relatively high absorption coefficient and the narrow direct bandgap energy (Junqiao, 2009). Remarkable improvement in growth strategies has resulted in a significant enhancement in its material property and growth of single-crystalline InN resulting in the revision of its band gap from 1.9eV to 0.7-0.8 eV (Wu et al., 2002). InN holds enormous potentials in various device applications including infrared photo detectors, ultrahigh speed transistors, Terahertz emitters (THz), lasers and solar cells (Ashraful Ghani et al., 2003). Despite these huge potentials, the successful growth of InN NRs has been very difficult due to its low decomposition temperature, very high indium (In) migration rate, high equilibrium vapour pressure of nitrogen over indium, (Chang et al., 2009; Chang et al., 2010), narrow InN growth temperature window coupled with highly critical influence of N/III ratio and lack of suitable substrates. Although various growth techniques including pulsed laser deposition (Ohba et al., 2009), hydride vapor-phase epitaxy (Zeghouane et al., 2020), sputtering (Sun et al., 2024), metal organic vapour phase epitaxy (MOVPE) and molecular beam epitaxy (MBE), have been explored for the growth of single crystalline InN materials, MOVPE and MBE have been the most successful and extensively studied (Imran et al., 2022, 2023; Johnson et al., 2004; Tessarek et al., 2016a, 2016b) with the growth of high-quality crystals of InN films. InN materials are generally grown at low temperature compared to other nitrides in order to prevent its dissociation. This conflicting demand of high temperature to crack NH_3 in MOVPE [otherwise known as metal organic chemical vapour deposition (MOCVD)] growth limits further development. Consequently, MBE has become a preferred alternative for the growth of high-quality InN due to its ability to independently set growth temperatures and generate nitrogen radicals from plasma sources(Nanishi et al., 2003). This enables growth at optimum growth conditions resulting from the independent control of growth and precursor temperatures in the absence of decomposition. On the other hand, one-dimensional nanorods (NRs) materials are a promising alternative to their bulk counterparts due to several advantages including large surface-to-volume ratio, large density of electronic states, diameter-dependent band gap, improved optical absorption and nearly defect-free structures when grown on foreign substrates(Hochbaum & Yang., 2010; Tchernycheva et al., 2007). Moreso, the use of nanostructured InN material such as InN NanoRod (NR) can improve the solar cell efficiency due to enhanced light absorption, photo-carrier collection, meanwhile the use of InN NRs will reduce the cost of the resulting solar cells because of the less materials used for the cells (less than half of the materials used in conventional solar cells).

Several substrates have been utilized for InN growth including sapphire, free standing GaN templates, GaAs, Si (100) and Si (111). However, the scalability, cleavability, low cost, relatively small lattice and thermal mismatch with InN, high-quality and availability in large sizes (up to 12 inches diameter) makes Si (111) substrate attractive for InN growth(Grandal et al., 2007). Given these obvious advantages of InN NRs growth on CMOS (complementary metal-oxide semiconductor) compatible and well-established Si technology (Anyebe, 2020) suitable for applications in integrated circuits, cost-effective and high-performance devices, there is need for extensive research activity to maximally exploit its advances over other substrates. This is in addition to the fact that there are limited reports (Feng et al., 2015; Sánchez-García et al., 2006; Shen et al., 2006), of the MBE growth of InN NRs on Si. The MBE growth of InN NRs on Si (111) substrate is reported.

MATERIALS AND METHODS

InN NRs were deposited on Si (111) substrates by plasma assisted MBE. To remove the surface native oxide, the substrates were first chemically cleaned using 10% hydrofluoric acid solution. Then, they were quickly loaded into the MBE system and out- gassed at high temperatures. A nitrogen plasma power of 270W was utilized for the growth while the beam equivalent pressure (BEP) for N and In were fixed at 7.0×10^{-5} and 2.0×10^{-8} mbar, respectively for a growth duration of ~1 hr. The In shutter was then opened for the deposition of a 5nm 2D equivalent layer to create favourable NRs nucleation sites, then the InN film growth commenced with the simultaneous supply of both In and N growth precursors at a temperature of 550 °C. The morphology of the as-grown sample was examined using a Sirion field emission gun scanning electron microscope (FEG-SEM). High resolution X-ray diffraction (HRXRD) was used for the structural investigation of the sample. Renishaw inVia Raman microscope equipped with an 830 nm laser was utilized for Raman investigation of the sample. To better understand the optical properties of the sample, Photoluminescence (PL) measurement was carried out using the 532nm line excitation wavelength from a Nneodymiumdoped yttrium aluminum garnet (Nd: $Y_3Al_5O_{12}$) laser with InGaAs detector.

RESULTS AND DISCUSSION

Figure 1 shows the SEM image of InN NRs confirming the successful growth of the nanostructures. The as-grown NRs with lateral dimension of 165-205 nm and height 50-85nm. Interestingly, they are vertically aligned and non-tapered. The NRs also possess low aspect ratio with relatively large diameters which is attributable to an enhanced lateral surface migration of Indium at a moderately high growth temperature. For a further increase in growth temperatures, InN films with micro grains morphology would usually emerge(Hsiao et al., 2005) due to a further increase in lateral In adatom migration. Note that this is highly dependent on other growth conditions such as the V/III ratio.

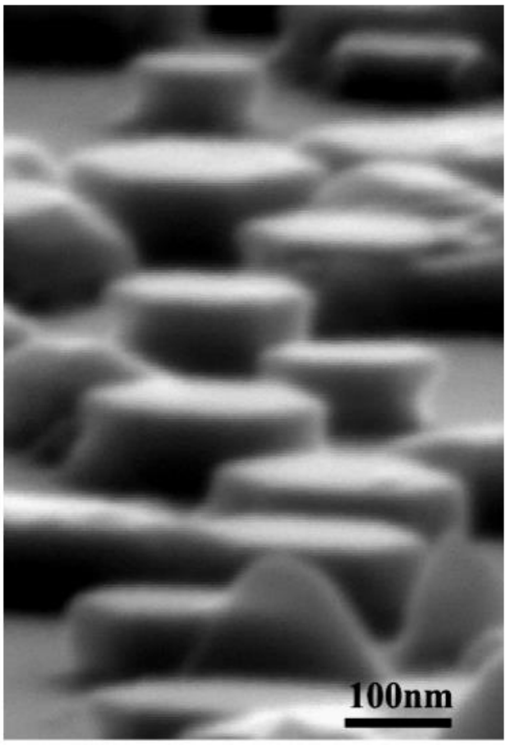

Figure 1:SEM images of InN Nanorods

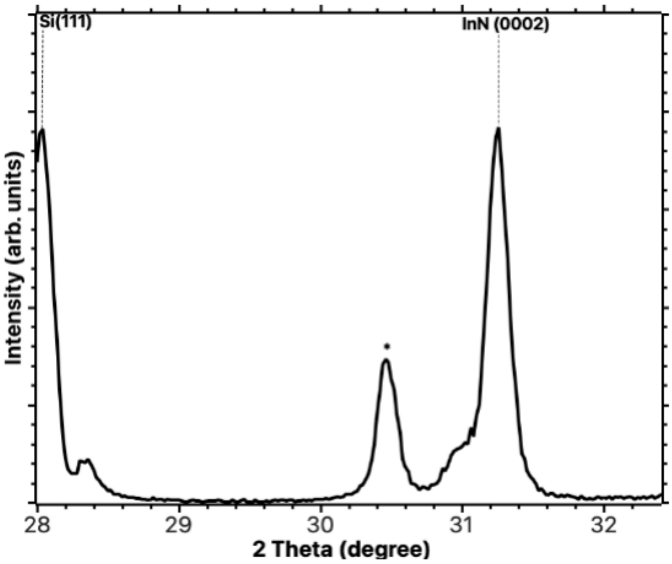

Figure 2: XRD of InN Nanorods

Figure 2 shows the XRD pattern of the NRs. The presence of the dominant (0002) diffraction peak with comparable intensity to the Si(111) peak indicates that the NRs are c-axis oriented, Wurtzite and single crystalline. The observable weak signal at around 30.5° can be attributed to the (222) peak of In_2O_3 (Chen et al., 2019a; Su et al., 2022; Tian et al., 2024; Zhang et al., 2022) resulting from the part oxidation of indium at moderately high temperature (Biju & Jain, 2009; Lee et al., 2007). The intensity of the (0 0 0 2) peak when compared to the low intensity In_2O_3 peak indicates that the NRs were preferentially grown along the [0001] direction. The small full width at half maximum (2 theta = 0.15°) indicates its high crystalline quality. These observations were further confirmed by room temperature macro-Raman spectrum (Figure 3). It has been reported(Agulló-Rueda et al., 2000) that zinc blende InN exclusively possess two Raman-active phonons modes F_2 (TO) and F_2 (LO) whereas Wurtzite InN display six Raman active phonons: A_1 (TO), A_1 (LO), E_1(TO), E_1(LO) and $2E_2$. Beside the broad peak at 520 cm^{-1} associated with the Si(111) substrate, four other active peaks positioned at 448cm^{-1}, 475cm^{-1}, 490 cm^{-1} and 585 cm^{-1} were observed and assigned to A_1(TO), E_1(TO)(Agulló-Rueda et al., 2000; Inushima et al., 1999)(Davydov, Klochikhin, et al., 1999)(Davydov, Emtsev, et al., 1999), E_2 (high) 489(Chen et al., 2019b)(Cheng et al., 2005), and A_1 (LO)(Davydov, Klochikhin, et al., 1999)(Davydov, Emtsev, et al., 1999) respectively as shown in Figure 3. The frequency of the A_1(TO) phonon at 448cm^{-1} is consistent with previously reported values (Davydov, Emtsev, et al., 1999)(Davydov, Klochikhin, et al., 1999)(Agulló-Rueda et al., 2000; Kim et al., 1996). Note that the E_1(TO) and the A_1(TO) are both forbidden for backscattering along the hexagonal *c*-axis [(Agulló-Rueda et al., 2000). The absence of conspicuous E_1(TO) and A_1(TO) peaks clearly indicates that the InN NRs were preferential grown along the c-axis which is in perfect agreement with the XRD result. Usually, the E_2 mode is sensitive to the strain in the c-plane. Wang et al(2006) determined the Raman frequencies of MBE grown strain free hexagonal InN of the E2 high and A1(LO) modes of InN epilayers to be 490.1 ± 0.2 and 585.4 ± 0.4 cm^{-1} respectively. The observation of both peaks at these frequencies for as-grown samples clearly demonstrates that the NRs are strain free and completely relaxed, which further corroborates the result of X-ray analysis.

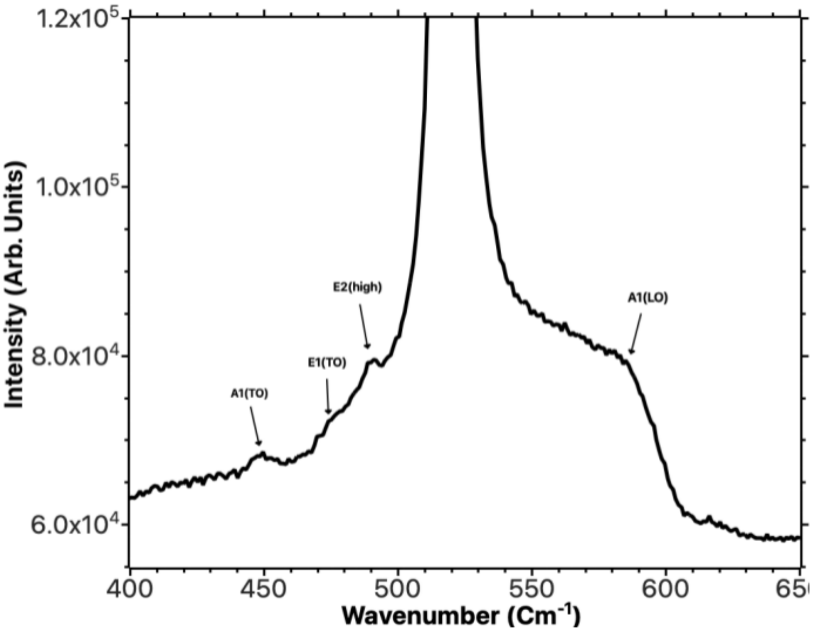

Figure 3: Raman of InN Nanorods

The 4K, PL spectra of the InN NRs is shown in Figure 4. Bright emissions at ~ 0.75eV (1.65µm) from the NRs are clearly visible which is in agreement with the revised energy band gap of single crystalline InN(Wu et al., 2002). This reveals the high crystalline quality and low defects concentration of the NRs.

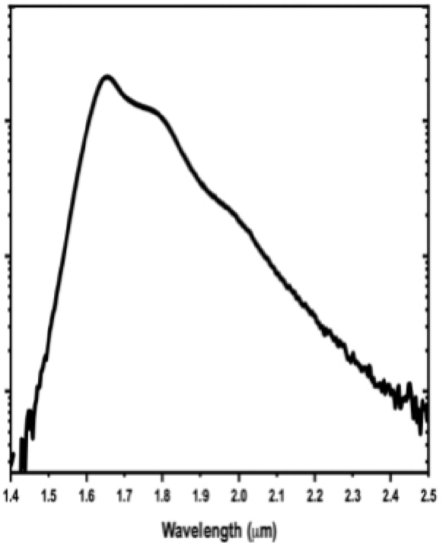

Figure 4: Photoluminescence of InN Nanorods

CONCLUSION

The growth of InN NRs on Si (111) by plasma assisted molecular beam epitaxy (PAMBE) have been investigated. X-ray and Raman studies have demonstrated that the NRs are single crystalline, Wurtzite and c-axis oriented. Bright PL emissions with a peak energy of 0.75eV was observed from the InN NRs indicating their high quality. This study unravels a strategy for the successful growth of high-quality InN NRs *on* Silicon which is highly promising for applications in next generation nanodevices.

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