Plasma synthesis of Indium Nitride Nanoparticles

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Abstract: While semiconductor nanomaterials of many types are making an impact on everyday applications, there continue to be nanomaterials that are difficult to synthesize but which offer great promise for technology. Plasma synthesis is a potential route to synthesizing some of these nanomaterials, for example Group III nitrides, which have unique optoelectronic properties. Here, we present a low-temperature plasma synthesis route to synthesis of indium nitride (InN) nanoparticles and explore the effects of changing plasma reactor parameters on the InN nanoparticle properties. For oxidation prone materials like indium, it is much easier for oxygen to displace nitrogen from the lattice structure and hence synthesis conditions need to be systematically explored to ensure stable InN. By tuning of power and flowrates we showed there is a shift from white indium oxide nanocrystals to black indium nitride. This opens up new paths in understanding the plasma reaction pathways during synthesis.

Keywords: Gallium nitride, Indium nitride, Nanocrystal, Plasma, Surface Chemistry

1. Introduction

Group III nitrides gained attention for optoelectronic devices from the late 1990s after the successful demonstration of blue emitting diodes in 1994[1]. Such has been the importance of group III nitrides that the Nobel Prize in physics in 2014 was awarded to I. Akasaki, H. Amano and S. Nakamura for their invention of efficient blue LEDs[2]. Silicon and other conventional semiconductors are not suitable for applications in the violet and blue region of the spectrum because of their lower band gaps. Nitrides like AlN (6.2 eV) and GaN (3.4eV) have high bandgaps and thus can operate in these regions.

While most of the early research was focused on GaN, InN has also seen growing interest. Bulk InN has a low bandgap of 0.7 eV. This enables alloying of GaN and AlN with InN to achieve a tunable bandgap over a wide range. Alloys of GaN and InN, also referred to as InGaN, have been used successfully in LEDs and lasers[3]. InN was shown to have the lowest effective mass for electrons amongst the nitride semiconductors resulting in high mobility and high saturation velocity[3]. The transport characteristics of InN were found to be much higher than GaN and GaAs over a wide range of temperatures[4]. For devices, these materials are commonly grown using CVD and other film-growth processes on substrates, but limitations related to the lattice mismatch of the material to the growth substrate, causing limitations in crystal quality as structural defects can form and propagate during epitaxial growth.[3]

Synthesizing freestanding nanoparticles of InN offers an intriguing workaround – they do not require any substrate for growth, and quantum confinement could lead to a tunable bandgap, opening interesting applications in the NIR.

Nonthermal Plasma synthesis of nanomaterials has been growing in recent years, due to the nanomanufacturing needs of a low temperature continuous process free of corrosive gases or organic solvents, while at the same time will allow for control over nanomaterial size shape and crystallinity. Nonthermal plasma synthesis has been shown to produce high quality nanocrystals of silicon, germanium, alloys, and some nitrides, phosphides and sulphides[5]–[13]. However, for many of these materials, the crystal structure is stable - meaning that while the surfaces may interact with the environment through oxidation or other reactions, the core of the nanocrystals remain stoichiometrically intact. InN presents a unique challenge in that it is relatively easy to oxidize *through the core even after synthesis*, meaning that the synthesis is not as straightforward as for many of the other materials. Here we present our results on the range of conditions required for synthesis of stable InN nanocrystals, in avoidance of bulk oxidation of the produced material.

2. Experimental Details

The synthesis of InN was carried out in a non-thermal plasma reactor (schematic in Fig. 1).



Exhaust to Vacuum

Fig. 1: Reactor schematic. Reaction gases were NH₃, Ar, and TMIn.

The precursor used was trimethyl indium (TMIn) Since the precursor is solid at room temperature, it was heated so that sufficient vapors are formed for gas phase synthesis. In addition to heating the precursor, stainless steel tubes upstream and downstream to the mass flow controller were also heated to avoid any deposition on the inside on the tubes. The quartz reactor diameter was 12.7 mm, and power was supplied via a triple electrode configuration (central powered electrode supplied with 13.56MHz RF power, and dual grounded electrodes upstream and downstream of the powered electrode). Flow rates for the precursors were kept below 1 sccm, argon was held constant at 60 sccm and ammonia at 65 sccm. The total pressure inside the reactor was around 4.9 Torr at the time of synthesis. After synthesis the particles were inertially impacted on glass substrates placed downstream of the reactor.

3. Results and Discussion

The synthesis conditions for the samples made are given in Table 1.

Sample No	TMIn Flowrate (sccm)	Power (W)	Color of nanoparticles
1	1	100	Black + White
2	1	50	Black
3	0.5	50	Black

50

White

0.2

4

 Table 1. Reaction conditions for synthesis

Experimental runs with conditions of sample #1 yielded a mixture of black and white deposition. While black nanoparticles are expected for this very-low-bandgap material (0.65-1.89 eV for InN [14]), the white deposition was unexpected. The deposition was characterized by XRD which is depicted in Figure 2. The XRD data showed peaks corresponding to (211), (222), (400), (440) crystallographic planes of indium oxide crystals along with other minor peaks. The obvious oxidation of the material can originate from two sources: oxygen present inside the reactor or oxidation when the sample is being taken out of the reactor after synthesis. Leak testing of the reactor before synthesis did not reveal any major breaches, and thus we concluded that oxidation likely occurs in the ambient air upon removal of the samples from the reactor. The Gibbs free energy per In atom for oxidation is -334.75kJ/mol as compared to -86kJ/mol for nitridation. In other words, the In-O bond is more stable than the In-N bond and thus oxidation is likely to occur if the opportunity is presented during exposure to air.



Fig. 2: XRD pattern from Sample #1, in which a black and white nanoparticle deposit was observed. The narrow peaks indicate a relatively large nano-crystallite size, and the peaks correspond to In_2O_3 crystallite reflections (referenced in black parentheses).

A second confirmation was that at the time sample 1 was being taken out from the reactor, the sample could be visibly seen oxidizing with a strong incandescence. The TEM images are shown in Figure 3. For the white deposition (Figure 3), distinct faceted morphology is observed while for the black particles (Figure 4), this faceting is more difficult to discern.



Fig. 3: Photo of sample after taking out of reactor (left); TEM images of white deposit (middle and right).



Fig. 4: TEM images of black deposit

Subsequently, we adjusted the synthesis parameters in an attempt to stop the sample from oxidizing. It was found that lowering the power to 50W and flowrate to 0.2 sccm of indium precursor resulted in a black sample – indicative of InN. XRD showed a broad peak centered around 31.2° , a low intensity peak around 52° and a shoulder around 62° . (Figure 5). TEM images showed clear lattice fringes confirming the presence of crystals (Figure 6).



Fig. 5: XRD pattern from Sample #2, a black deposit of nanoparticles. The broadened peaks correspond to nanocrystallites of InN (reference reflections shown in black).



Fig. 6: TEM images from Sample #2.

4. Conclusions

In conclusion, we have shown that by changing the reactor parameters (namely, reactor power), air-stable InN nanoparticles can be synthesized in a nonthermal plasma reactor. We hypothesize that the elemental stability is attributed to reduction of dangling bonds on the surface,

which may have increased incidence upon higher power to the reactor. Our future work will focus on size-tunability of these nanoparticles and using in-situ diagnostic methods such as optical emission spectroscopy and electrical probes to understand the local environment of the InN nanoparticles during synthesis.

5. References

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