MOCVD Growth of Indium Nitride

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ABSTRACT

Investigation on the growth of indium nitride films has been reported in this paper. By utilizing a new double-zone MOCVD reactor, high growth rate of good quality InN films from trimethyalindium (TMIn) and ammonia precursors has been demonstrated. Characterization techniques including scanning electron microscope (SEM), x-ray diffraction (XRD), and Raman spectroscopy were applied to evaluate the quality of the films. While SEM and XRD showed highly smooth, single-phase InN film deposited without indium droplet aggregation, the Raman spectroscopy showed broad peak besides the InN signatures, indicating rooms for further improvement.

INTRODUCTION

Indium nitride (InN), a III-V compound semiconductor with a stable wurtzite crystal structure and a direct band gap of ~1.9 eV, is highly desirable.(1) The non-toxic constitutions and easy recycling of the material, in particular, make indium nitride ideal for environmentally safe and sustainable applications. However, MOVPE growth of InN is difficult due to its easy dissociation at elevated temperatures. This limits the growth process under 550°C, which cause indium droplet formation in the films due to the deficiency of nitrogen at such temperature. Various attempts were made to ravel this problem including utilizing additional microwave power to crack N_2 at a low pressure,(2,3,4) and a high NH_3 partial pressure to provide enough atomic nitrogen under 500°C, which substantially improved the film quality.(5,6) Nevertheless, the aforementioned approaches suffered from either low-growth rate or large consumption of high purity NH_3 and made the processes expensive. Meanwhile, growth of high-quality

InN films is restricted due to the lack of lattice-matched substrate. A recent report utilizing appropriate nitridation of sapphire substrate in an MOVPE process substantially reduced the mismatch.[7] A low cost, high growth rate process for InN is highly desirable for applications such as visible optoelectronics and high efficiency solar cells. In this paper, we reported high-quality InN films deposition using a novel designed MOCVD on a (0001) sapphire substrate at a considerably high growth rate of 2.4 μm/hr.

EXPERIMENTAL

As shown in the schematic diagram in Figure 1, a double-zone MOCVD reactor with temperature controlled by two susceptors, a high temperature one above 700 °C inside the RF coil for NH_3 cracking and a lower temperature one partially into the RF coil to maintain the growth temperature of 500 °C. Trimethylindium (TMIn) was carried by nitrogen gas with a flow rate of 10 sccm and mixed with additional 200 sccm nitrogen flow before arriving the substrate. NH_3 flow of 1000 sccm went through the high temperature zone and mixed with the TMIn on the top of the substrate surface. Before the growth, the sapphire substrate went through a nitridation process at 1000 °C under NH_3 atmosphere for 60 minutes. The substrate temperature was then lowered down to 500 °C and the InN growth started. The resultant films were characterized by XRD using a Rigagu D/MAX C diffractometer. The surface morphology and cross section of the samples were studied using a Hitachi S800 scanning electron microscope (SEM). Raman spectra were obtained through a Renishaw system 2000 micro-Raman spectrometer with a He-Ne laser as the light source.

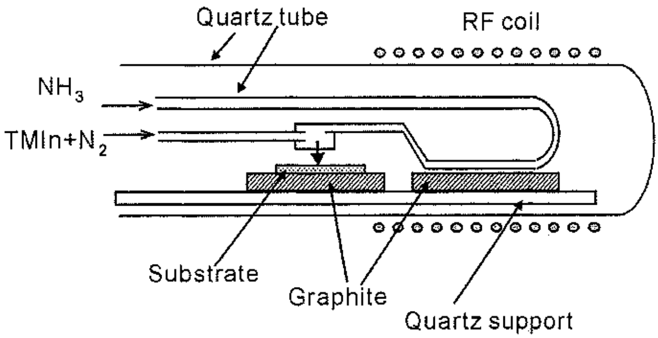

Figure 1. Schematics of the double-zone MOCVD reactor.

RESULTS AND DISCUSSION

The resultant film was black but mirror-like with barely roughness observable through an optical microscope of magnification 500. Small but tightly connected bumps were however observed in the SEM plane view image (Figure 2(a)). The average roughness was about 50nm as seen from the cross section view in Figure 2(b). The 1.2 μm film thickness gives a growth-rate of 2.4 μm/hr, which is much larger than the reported either in a microwave-excited MOVPE of 0.3μm/h or in a plasma-assisted MOCVD growth of 200nm/hr.[8,9]

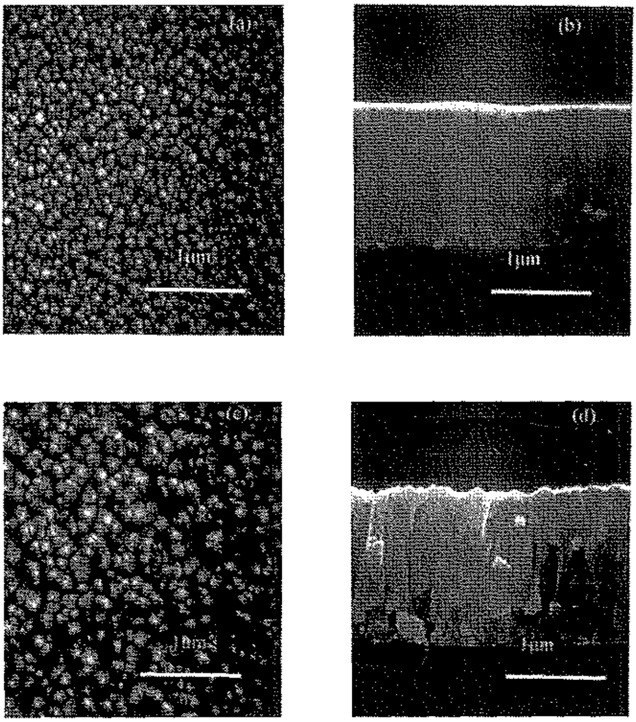

Fig. 2. SEM images of InN growth on sapphire (0001) with different TMIn carrier gas flow rates: (a)plane view (10 sccm), (b)cross section (10 sccm), (c)plane view (14 sccm), (d)cross section (14 sccm).

The film morphology is very sensitive to substrate temperature and III-V gas ratio of the growth. For example, Figure 2(c) and 2(d) show the plane view and cross section of another film at the same growth condition except for a larger TMIn flow rate of 14 sccm. In such condition, columnar growth of the film occurred and larger roughness was observed on the surface. Although the growth rate reached 3 μm/hr, a trade off must be made between the growth rate and the quality of the films. In many cases when the growth condition was slightly off, indium droplet occurred in the films, which is mainly attributed to the deficiency of atomic nitrogen in the process. A dilemma between dissociation of the film itself at higher deposition temperature and indium droplet aggregation in the film at lower temperature always exist for the growth of InN. It turned out that the window for good quality growth is very narrow. Small change of the III-V gas ratio or shift of the substrate temperature can be traumatic to the quality of the films.

As shown in Fig. 3, typical θ-2θ XRD scan showed InN (0002), InN (0004) and sapphire (0006) at 31.7°, 65.2° and 41.6°, respectively, indicating oriented growth of (0001) hexagonal InN on the (0001) sapphire substrate. The spectrum in Figure 3 is much neater than our earlier results, in which other components such as indium droplets also appeared. The lattice constant thus obtained from Figure 3 is estimated to be 5.710 Å, which is within the reported values ranging from 5.68 to 5.73 Å.

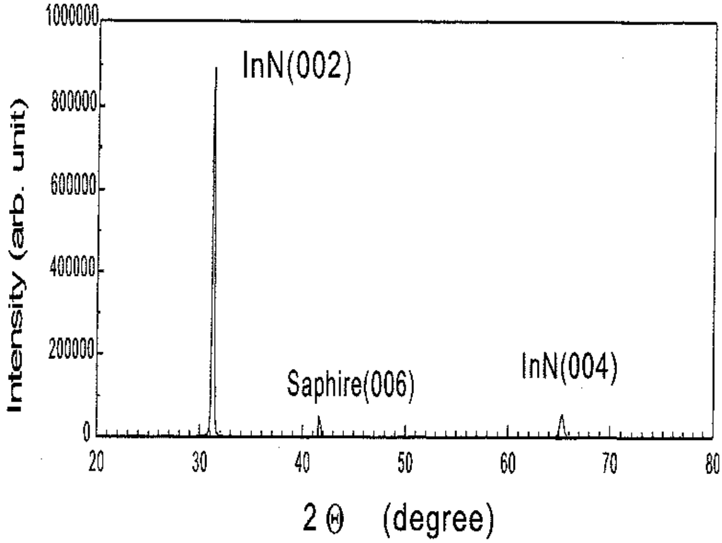

Figure 3. XRD θ–2θ scan of the InN/sapphire layer.

Fig. 4 shows the Raman spectrum of a typical InN film. The h-InN related mode at 495 cm^{-1} (E_2 mode) could be clearly identified.[10,11] The 596 cm^{-1} A_1 (LO) mode, however, is broadened and shifted toward lower wavenumber. Similar observation was also reported in InN growth at a lower substrate temperature.[12] The Raman spectrum indicates that there are rooms for further improvement of the film quality. Better choice of the lattice-matched substrate and proper utilization of buffer/nitridation layers may result in epitaxial growth of the InN films.

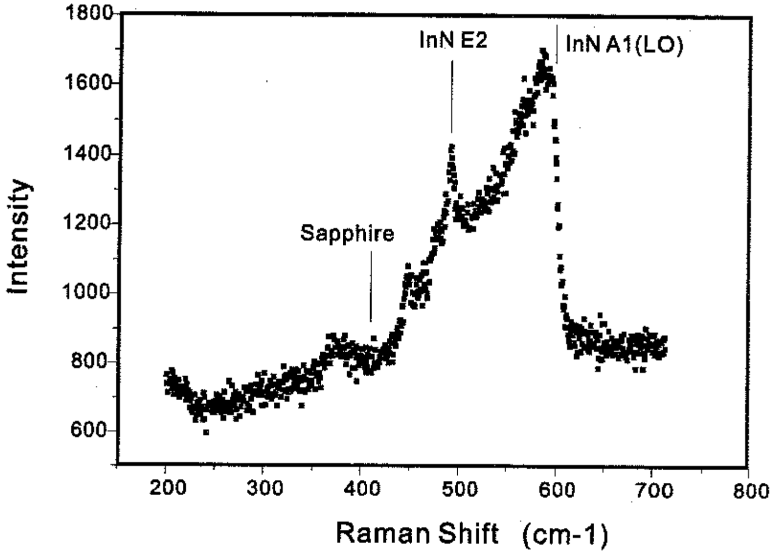

Figure 4. Raman spectra of the InN/sapphire layer.

CONCLUSION

It has been demonstrated that the reported double-zone MOCVD method produced good quality InN films at a relatively high growth rate much higher than other reports in the literature. XRD, SEM characterization indicated highly smooth, single phase, oriented films deposited. Further improvement of the film quality by choosing different substrate to accommodate the lattice mismatch and/or choice of proper buffer/nitridation layers to enhance the epitaxy is underway. On the other hand, other studies such as photoluminescence and doping will be implemented to investigate possible optoelectronic applications of the films.

ACKNOWLEDGEMENTS

Financial support from the Institute of Atomic and Molecular Sciences, Academia Sinica, and discussion with professor M.C. Lin is gratefully acknowledged.

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