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Single-crystalline InN films with an absorption edge between 0.7 and 2 eV grown using different techniques and evidence of the actual band gap energy

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Single crystalline InN films with an absorption edge between 0.7 and 2 eV have been grown using a variety of different techniques including; conventional metal-organic vapor-phase epitaxy (MOVPE), ArF-laser assisted MOVPE (pa-MBE), and plasma-assisted molecular-beam epitaxy. Analysis of samples grown using different methods has led to important evidence for determining the actual band gap energy of InN. In an effort to find the origin of the change in absorption edge, this evaluation was focused on the la-MOVPE of InN. This deposition technique enables InN film deposition over a wide range of growth temperatures, ranging from room temperature to a very high temperature (700 °C). Characterization of InN films grown over a wide range of temperatures strongly suggests that oxygen contamination leads to a larger band gap absorption energy value than the actual value, even in the case of single crystalline films. In films grown at low temperatures, oxygen appeared to form an alloy, resulting in a larger absorption edge, whereas, in films grown at high temperatures oxygen was present as a donor, which resulted in a larger absorption edge due to a Burstein–Moss shift. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1632038]

Indium nitride (InN) is a highly attractive III-nitride semiconductor with numerous potential applications.[1] In recent studies, the band gap energy of InN has become the focus of InN research. Early studies of InN films suggested a direct band gap of ~2 eV.[2,3] Very recently, optical characterizations of high quality InN films grown using molecular-beam epitaxy (MBE) and metal-organic vapor-phase epitaxy (MOVPE) have revealed that the actual band gap energy of InN is about 0.7 eV at room temperature.[4–8] These contradicting values for the actual band gap energy of InN have led to further investigation of the actual band gap value. The current research on this subject indicates that the optical band gap energy of InN is close to 0.7 eV. The explanation for the existence of a range for the band gap energy, the most fundamental optical property, has yet to be elucidated and remains a topic of debate among scientists. Although explanations including the incorporation of oxygen and the Burstein–Moss shift have been proposed, the actual roles of these effects have not been clarified.

Herein, the causes of this significant variation in the band gap value of InN are clearly reported. The elucidation of the cause was accomplished by growing single crystalline InN films with an absorption edge between 0.7 and 2 eV using a number of different techniques. Oxygen contamination in InN films was thought to be responsible for a larger band gap value, even in a single crystalline film. In the films grown at low temperatures, oxygen incorporation was significantly enhanced, and appeared to form an alloy, with a larger absorption edge energy. Whereas, in the films grown at high temperatures, oxygen existed as a donor and resulted in a larger absorption edge energy due to a Burstein-Moss shift.

InN films were grown on (0001) sapphire substrates using conventional MOVPE, ArF-laser assisted MOVPE (la-MOVPE), and plasma-assisted MBE (pa-MBE). The MOVPE films were grown at 450 to 650 °C under a pressure of 76 and 760 torr using NH_3 and TMI. The la-MOVPE films were grown at room temperature to 700 °C under a pressure of 0.1 to 10 torr using NH_3 and TMI. A 193-nm wavelength laser beam, generated from an ArF excimer laser, was radiated directly above the substrate region, with output energy of about 50 mJ/pulse and a repetition rate of 20 Hz during the growth period. The pa-MBE grown films were grown at 450 to 580 °C. An In flux was produced using a conventional K-cell, and decomposing N_2 gas in a rf-plasma cell generated nitrogen radicals. The crystallinity (single or polycrystals) of all of the samples was determined by reflection high-energy electron diffraction as well as by x-ray diffraction analysis. The carrier concentration and mobility were determined using the Hall measurement, and all the films grown were determined to be n-type. The MOVPE grown films were single crystalline films with a carrier concentration of 10^{18} to 10^{20} cm^{-3} and a Hall mobility of 200 to 700 cm^2/Vs. The la-MOVPE films were composed of both polycrystalline and single crystalline films with a carrier concentration of 10^{20} to 10^{21} cm^{-3} and a Hall mobility of 5 to 100 cm^2/Vs.

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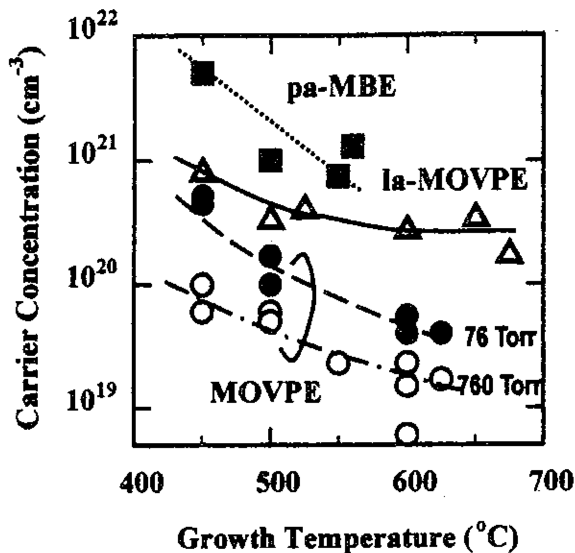

FIG. 1. Growth temperature dependence of the carrier concentration in the InN films grown byMOVPE, la-MOVPE, and pa-MBE.

The pa-MBE grown films were single crystalline with a carrier concentration on the order of 10^{21} cm^{-3} and a Hall mobility of 20 to 80 cm^2/Vs. The optical absorption edge energy was measured at room temperature with a double monochrometer optical system (Perkin Elmer, Lambda 19) and the composition was analyzed using x-ray photoelectron spectroscopy (XPS), for all of the films grown.

The growth temperature dependence of the carrier concentration in the InN films grown by MOVPE, la-MOVPE, and pa-MBE is shown in the Fig. 1. Similar trends with respect to growth temperature dependence were observed in all of the growth techniques, the carrier concentration increased with decreasing growth temperature. The absorption edge values for the single crystalline InN films grown by MOVPE, la-MOVPE, and pa-MBE as a function of the carrier concentration are shown in the Fig. 2. The data shown here was obtained for InN films grown at a relatively high temperature; 500 to 650 °C for MOVPE and la-MOVPE, and 550 to 580 °C for pa-MBE. Also shown in the figure is data for polycrystalline and single-crystalline films reported by other groups, and the relationships between absorption edge energy and carrier concentration derived by Tansley and Foley,[3] Davydov *et al.*,[4] and Wu *et al.*[9] As shown in the Fig. 2, all of the data is clearly divided into two groups; polycrystalline and single-crystalline. Polycrystalline samples show a small carrier-concentration dependence on absorption edge, similar to the behavior of indium oxy-nitride ($InNO_x$).[10] On the other hand, single-crystalline samples show a change markedly different from that of polycrystalline samples. A large change, from 0.7 to 2 eV, has been observed in the absorption edge of single crystalline InN film at a carrier concentration range of 10^{18} to 10^{21} cm^{-3}. This change is in good agreement with the Burstein–Moss shift predicted by Davydov *et al.*[4] and Wu *et al.*,[9] as shown in the Fig. 2.

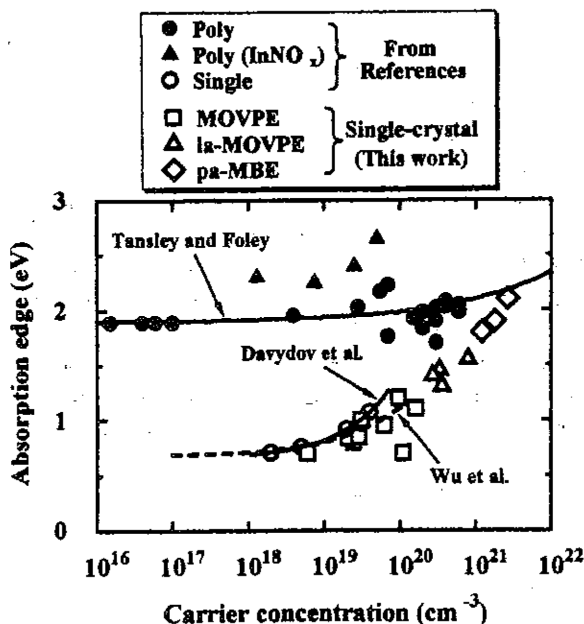

FIG. 2. Absorption edge values for different InN films as a function of the carrier concentration.

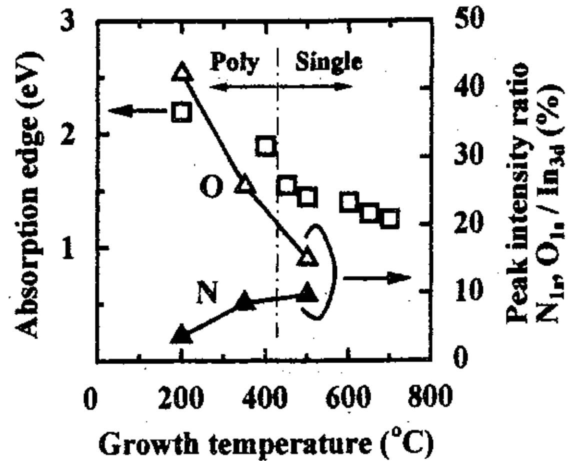

FIG. 3. Growth temperature dependence of the absorption edge and XPS N_{1s} and O_{1s} peaks intensity ratio compared to In_{3d} for the InN films grown by la-MOVPE.

The study is focused on the la-MOVPE InN in order to further clarify the cause of the change in absorption edge. The la-MOVPE growth technique enables InN film deposition over a wide range of growth temperatures, from room temperature to a very high temperature (700 °C).[11] Early studies of InN, which suggested a direct band gap of ~2 eV were carried out in the polycrystalline films grown at very low temperatures. Therefore, films grown by la-MOVPE at very low temperatures up to a very high temperature were studied. The absorption edge for the la-MOVPE samples was observed to show a marked dependence on the growth temperature. Figure 3 shows the growth temperature dependence of the absorption edge for la-MOVPE InN samples. In addition, the figure shows the XPS N_{1s} and O_{1s} peak intensity ratio compared to In_{3d} for the InN films grown by la-MOVPE at different temperatures. As seen in the figure, the absorption edge increases from 1.3 to more than 2 eV, as the growth temperature is decreased from 700 to 200 °C. A polycrystalline film grown at 200 °C has an absorption edge of ~2 eV. XPS spectral signals for N_{1s} and O_{1s} show that the N content decreases and the O content significantly increases with decreasing growth temperatures, suggesting that the incorporation of oxygen is responsible for the increase in absorption edge. The increase of oxygen is also reflected in the carrier concentration, as the carrier concentration markedly

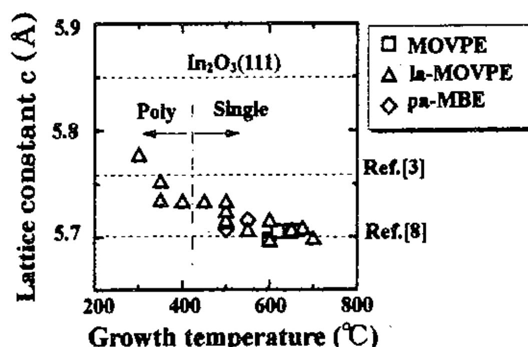

FIG. 4. Lattice constant c measured for InN films grown at different temperatures using the different techniques.

increased with decreasing growth temperature, as shown in the Fig. 1. In an effort to confirm these findings, the InN film was grown by la-MOVPE at room temperature. The color of the grown film was yellow ($\sim$2.2 eV), but the color was observed to disappear immediately after the samples were exposed to the atmosphere, and the film became transparent. It seems that the film is highly oxidized leading to the formation of optically transparent $InN-In_2O_3$ alloys.[8] These observations suggest that as the growth temperature is decreased, the films become increasingly oxidized, and have a higher absorption edge. This is thought to be due to the possibility that either with lowering growth temperatures, the In and N bond formation decreases, which thereby enhances the In and O bond formation, or, in InN films grown at lower temperatures, In prefers bonding with O.

As detailed above, InN films can have a larger band gap if the film is grown at low temperature, the film is polycrystalline, and the carrier concentration is very high. In order to more clearly understand the mechanism and the reason that films grown under these conditions have a larger band gap, the crystalline parameter was evaluated. Figure 4 shows the lattice constant c measured for InN films grown at different temperatures using different techniques. It is clear that the samples grown at a relatively high temperature (or in a single crystal) have a lattice constant very near to that for the high quality InN films reported by Davydov *et al.* (5.70 Å).[8] Whereas, the la-MOVPE samples grown at a low temperature ($\sim$300 °C) have a lattice constant very similar to that previously reported by Tansley and Foley (5.76 Å).[3] These findings indicate a trend towards In_2O_3 formation with decreasing growth temperature, as shown in the Fig. 4. The increase in the lattice constant, with decreasing growth temperature, reflects the increase in oxygen content in the films, toward the formation of In_2O_3. This suggests that in the case of low temperature grown films, oxygen easily forms an alloy with InN, and the variation in oxygen content due to growth temperature is reflected in the lattice parameter, and in the absorption edge. However, with high temperature grown, or single crystalline InN films, there was no significant change in the lattice constant c, while a large change in the absorption edge 0.7 to 2 eV was observed at a carrier concentration range of 10^{18} to 10^{21} cm^{-3}. This finding suggests that in the case of high temperature grown films, oxygen exists as a donor and does not form an alloy. Thus, there is no change in the lattice parameters, but the large change in the absorption edge observed was attributed to the Burstein–Moss shift. It is important to note that the pa-MBE and la-MOVPE deposited films, which have a relatively high percentage of oxygen, showed a very high carrier concentration, as seen in Fig. 1, and therefore a very large absorption edge ($\sim$2 eV) was observed, even in the single-crystalline film. The MOVPE InN films grown under low pressure have a high carrier concentration, whereas la-MOVPE films are grown in under very low pressure ($\sim$1 torr) and therefore have very high carrier concentration, as shown in Fig. 1. The pa-MBE deposited samples had a relatively high level of oxygen derived from the plasma cell and showed a very high carrier concentration. The plasma cell used in this study consisted of a quartz (SiO_2) tube, which easily contaminates oxygen. A high level of oxygen was also observed in the GaInAsN films grown using the same pa-MBE technique. This was confirmed by secondary-ion-mass spectroscopy analysis.

In conclusion, the causes of change for the band gap value of InN were investigated using several different growth techniques. Single-crystalline InN films with an absorption edge between 0.7 and 2 eV were grown. Oxygen contamination in the InN grown film was found to be a cause of a larger band gap absorption energy value even in the case of single crystalline film. In low temperature grown films, oxygen incorporation was significantly enhanced and seemed to exist as an alloy, which caused a larger absorption edge. Whereas, in films grown at higher temperatures, oxygen existed as a donor and caused a larger absorption edge due to a Burstein–Moss shift. This evaluation enabled the conclusion that the actual optical band gap energy of InN is about 0.7 eV.

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