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SOME PROPERTIES OF InN FILMS PREPARED BY REACTIVE EVAPORATION

J. W. Trainor* and K. Rose

Rensselaer Polytechnic Institute

Troy, New York 12181

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Some optical and electrical properties of degenerate InN films prepared by a reactive evaporation technique are presented. Thermal stability of these easily dissociated samples is discussed and evidence is presented indicating that the partial pressure of atomic nitrogen rather than diatomic nitrogen is a more fundamental parameter for describing thermal equilibrium. This has important implications for the growth of all group III-nitrides.

Key words: InN, Reactive Evaporation, Atomic Nitrogen, Thin Films, Optical Absorption, Transport Properties, Thermal Stability.

*J. W. Trainor is now with the Xerox Corporation, 800 Phillips Road, Webster, New York 14580.

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Introduction

Indium nitride films have been prepared by evaporating indium in an atomic nitrogen atmosphere (1,2). Samples were prepared from 25 to 380° C with growth rates ranging from 1.5 to 12 microns/hr. The resulting material demonstrated n-type behavior with electron concentrations in the 10^{20} cm^{-3} range. This presumably degenerate material had a room temperature Hall mobility of 20 cm^2/V-sec.

Optical absorption studies show behavior similar to that reported by Hovel and Cuomo (3) for reactively sputtered material. Annealing studies were conducted and thermal stability of the samples under seemingly unstable thermodynamic conditions suggests that high atomic nitrogen pressures during growth is fundamental to growing stoichiometric material. This has strong implications for the growth of nitrides by evaporation, sputtering, and chemical vapor transport.

Sample Preparation

Indium nitride samples have been prepared by electron beam evaporation of indium onto heated substrates in an atomic nitrogen environment. (Growth in an environment containing atomic nitrogen has been reported for GaN (4,5)). The latter was provided from a continuous flow pulsed nitrogen plasma that was expanded into the evaporation system and directed onto the substrate. Although various excited levels of both atomic and diatomic nitrogen are created in the plasma region, appropriate precautions insured that only ground state species entered the evaporation system. Typical evaporations were carried out with an atomic nitrogen impingement rate of 10^{18} atoms sec^{-1} cm^{-2} in the deposition region.

High purity indium (99.99%) was used for all films. Samples were prepared on 0001 sapphire at temperatures ranging from 25 to 380° C. Typical growth rates ranged from 1.5 to 12 microns/hr. The reactively evaporated films were always smooth and demonstrated a silver lustre when viewed in reflection. Transmitted light appeared red or red-brown depending upon thickness.

Fundamental Edge Absorption

Optical characterization of InN films was performed. They are presented in Figure 1 for typical films along with Hovel and Cuomo's (3) results for sputtered InN. As with GaN (1), the absorption coefficient increased with increasing preparation temperature. This is attributed to increased crystallite size and crystal order with increasing growth temperature.

Note that the absorption of films of this study is shifted to 0.1 eV higher energy than that found in sputtered layers. It is felt that this shift is a direct result of degeneracy. Absorption dependence of this nature was first interpreted by Burstein (6) and is most pronounced in semiconductors having small effective masses since they possess a small density of states and degeneracy occurs at low doping levels. In such cases, the absorption edge shifts to higher energy with increasing doping. Note from Figure 1 that increasing absorption edge energies are associated with increasing carrier concentration.

The sharp absorption edge occurring at low energies in Figure 1 is due to free carrier absorption. In these InN films this edge was extremely sharp and quite pronounced in comparison to GaN films.

An exponential variation of absorption with characteristic energy E_o,

$$\alpha = \alpha_o \exp(h\ /E_o) \qquad (1)$$

is indicated for this study. For the fundamental edge, experimental values of E_o were found to be 1.7 eV and 124 meV above and below the knee respectively. The low energy absorption of InN is also exponential with a characteristic energy of -90 meV. All of these values are in good agreement with those reported for sputtered material(3). The similarity in the shape of the fundamental absorption edge to that of GaN (1) suggests that the band structure of InN and GaN are the same. Specifically, InN is probably a direct bandgap semiconductor.

The position of adjacent interference peaks coupled with independent thickness measurements shows that the samples have an index of refraction of approximately 2.9. This value may be in error by about 10 percent because of

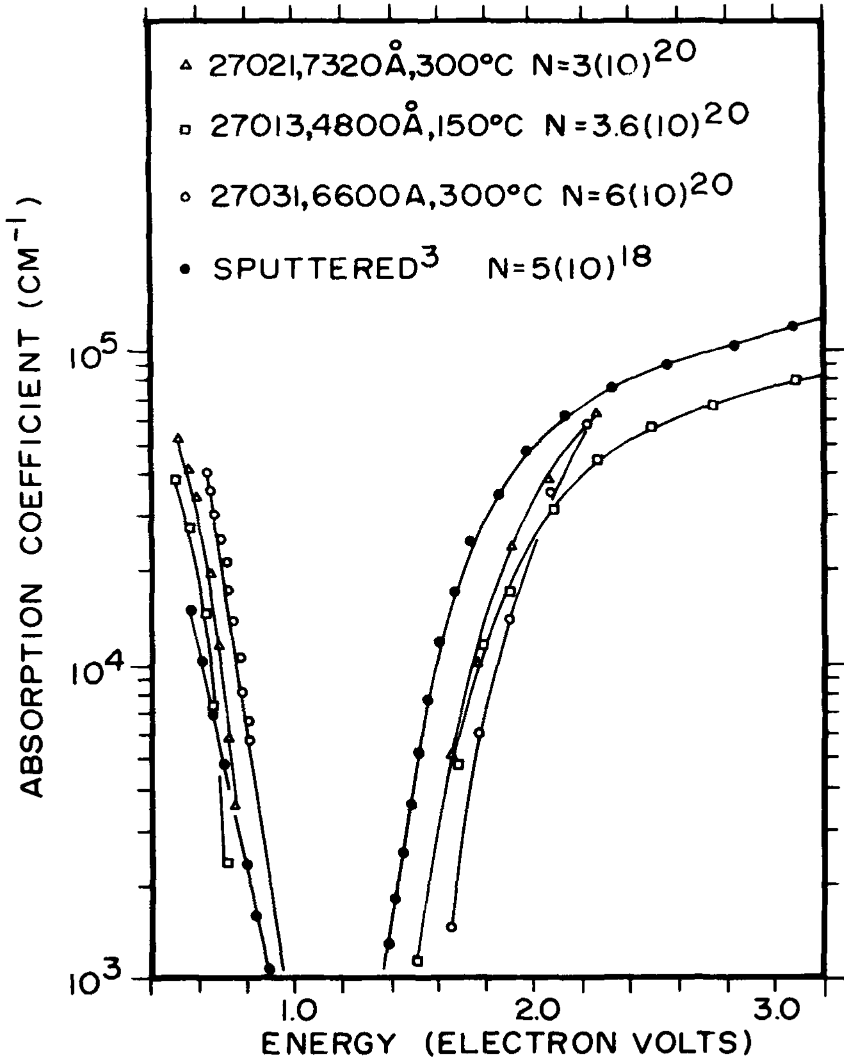

Fig. 1 InN Absorption Characteristics

shifts in the interference positions near the absorption edges. This value is also in good agreement with that reported for sputtered material (3).

Electrical Properties

InN samples were grown at temperatures of 25 to 380°C with growth rates ranging from 1 to 12 microns/hr. All samples were high conductivity n-type. Samples grown at the higher growth rates demonstrated very low Hall mobilities due to a higher density of native defects (scattering centers) and an increased number of grain boundaries. The best material (grown at 380° C at 1 micron/hr.) had a room temperature Hall mobility of 20 cm^2/V-sec and a carrier concentration in the 10^{20} cm^{-3} range. Hovel and Cuomo (3) reported Hall mobilities as high as 250 cm^2/V-sec for sputtered InN having carrier densities of 10^{18} cm^{-3}. This sputtered material may have been grown at temperatures as high as 600° C.

InN films grown in this study are thought to have both higher impurity density (due to indium agglomerates) and smaller crystallite size compared to sputtered material (3). Nucleation and growth theory support the observation that the best films were obtained at the highest growth rate. It would appear that even better films could be achieved by growth at higher temperatures (perhaps as high as 600° C) and lower rates. The magnitude of growth rate variations during growth was quite large for the case of indium and was attributable to difficulties in controlling the electron beam source.

Thermal Stability

Annealing studies were attempted with several InN samples in N_2 (standard pressure) at 500° C. In all cases, samples decomposed in a few minutes leaving an indium residue. It was found, however, that if samples were heated to 500° C (up to one hour) in an atomic nitrogen atmosphere (10^{-3} torr) they did not decompose. This latter annealing was carried out in the reactive evaporation growth system. Annealed samples showed only slight changes over their as-grown characteristics.

The stability of the InN films under these seemingly unstable thermodynamic conditions is attributed to the presence of atomic nitrogen over the sample surface. Stability of a solid compound in relation to its highest vapor pressure constituent is usually expressed by its equilibrium pressure/temperature relationship. For the nitrides (e.g., InN), the equilibrium gas pressure measured is that of diatomic nitrogen. However, the above experimental observations suggest that the pressure of the atomic species is the more fundamental parameter. This implies that the solid phase will remain stable at any given temperature provided that the atomic nitrogen pressure exceeds some specific value. Although stable conditions can be obtained by thermal dissociation of N_2 it is important to realize that other methods of increasing the N pressure exist: for example, ionization in a plasma. Thus, whenever a sufficiently high partial pressure of atomic nitrogen is generated over the sample by methods other than thermal dissociation, InN remains stable at significantly higher temperatures. This has strong implications for the growth of many nitrides and suggests that growth techniques usually discounted for nitride growth because of the excessively high temperature requirements can be utilized if sufficient (not necessarily thermal) means are provided for increasing the atomic nitrogen pressure.

Free Carrier Absorption

A sharp absorption below the fundamental edge that increased with increasing wavelength was observed in all InN samples. As with GaN, this was attributed to free carrier absorption. Data for a typical sample is presented in Figure 2. The curve was always found to have slope equal to 6.8. However, this value is not indicative of any of the conventional scattering mechanisms (i.e., phonon, polar, or impurity scattering).

The nature of this unusual transition is not understood. However, such an abrupt absorption might result from transitions between conduction subbands. Additionally, the degeneracy of the InN samples suggests that electron concentrations (of order 10^{20} cm^{-3}) are sufficiently large to cause electron-electron scattering to be significant. The slope dependence of this scattering mechanism is not known.

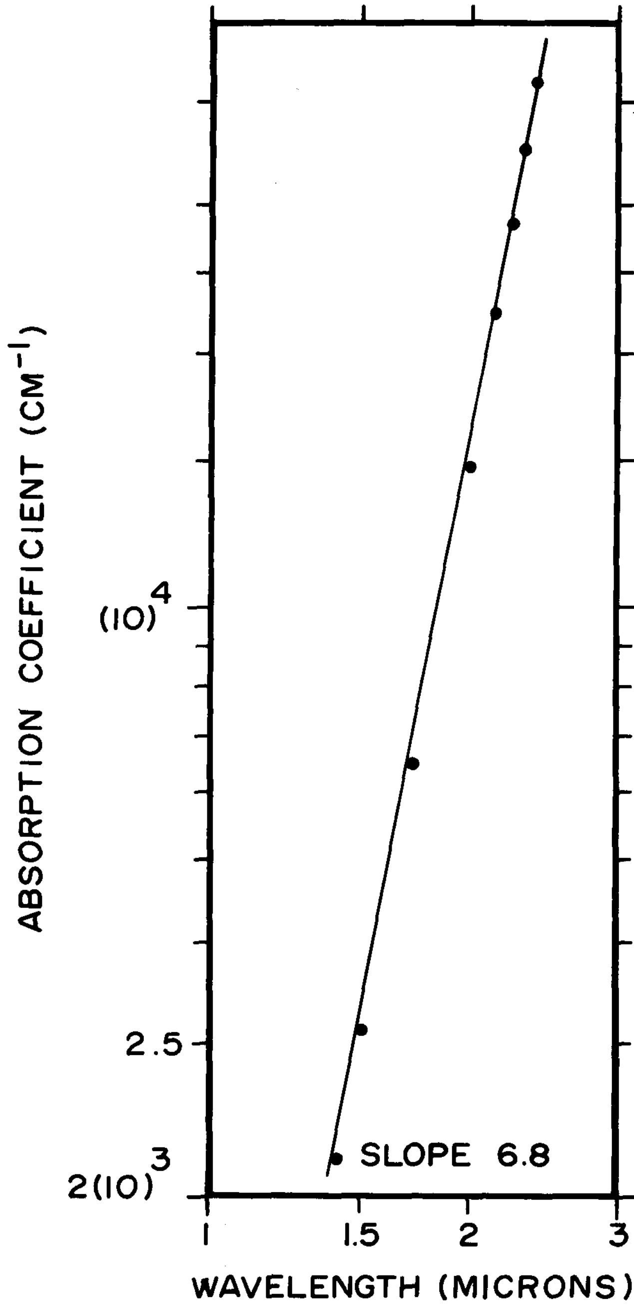

Fig. 2 InN Free Carrier Absorption

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