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Effects of electron concentration on the optical absorption edge of InN

J. Wu and W. Walukiewicz[a)]
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

S. X. Li, R. Armitage, J. C. Ho, E. R. Weber, and E. E. Haller
Materials Sciences Division, Lawrence Berkeley National Laboratory, and Department of Materials Science and Engineering, University of California, Berkeley, California 94720

Hai Lu and William J. Schaff
Department of Electrical and Computer Engineering, Cornell University, Ithaca, New York 14853

A. Barcz and R. Jakiela
Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland

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InN films with free electron concentrations ranging from mid-10^{17} to mid-10^{20} cm^{-3} have been studied using optical absorption, Hall effect, and secondary ion mass spectrometry. The optical absorption edge covers a wide energy range from the intrinsic band gap of InN of about 0.7 to about 1.7 eV which is close to the previously accepted band gap of InN. The electron concentration dependence of the optical absorption edge energy is fully accounted for by the Burstein–Moss shift. Results of secondary ion mass spectrometry measurements indicate that O and H impurities cannot fully account for the free electron concentration in the films. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1704853]

InN is an important component of the widely used group III-nitride alloys. However, it is also the least studied end-point compound of these alloys. Until recently, the band gap of wurtzite InN had been believed to be about 2 eV. This value was determined from the optical absorption edge of sputter-grown InN films which had high electron concentrations ($>10^{19}$ cm^{-3}) and low electron mobilities (<100 cm^2/Vs).[1,2] Recent experiments performed on high-quality InN films grown by molecular-beam epitaxy (MBE) have shown unambiguously that the fundamental band gap of InN is about 0.7 eV,[3,4] which is almost three times smaller than the previously accepted value. The origin of this large discrepancy is still unclear. Explanations that have been proposed include: free electron induced Burstein–Moss shift,[5] formation of large-band-gap indium oxynitride in the sputter-grown films, and quantum-size effects in InN nanocrystals that could raise the gap energy.[3]

In this letter we present systematic studies of InN films grown by MBE that show various optical band gaps ranging from 0.7 to 1.7 eV. The increase in the optical band gap is closely correlated to an increase in free electron concentration. We show that the shift of the absorption edge can be fully explained by the Burstein–Moss effect. We also discuss the relation between the electron concentration and the concentrations of O and H determined by secondary ion mass spectrometry.

Two sets of InN films were grown on sapphire substrates by MBE in two different laboratories. Details of the growth for sample set I were reported in Ref. 6. The InN layer thickness ranged from 200 nm to 7.5 μm.[6] The second sample set (set II) was prepared by dc plasma-assisted MBE at substrate temperatures from 450 to 550 °C and growth rates of ~0.3 μm/h, yielding InN layers of thickness 0.5–1.0 μm. For the set II films the nucleation procedure began with sapphire nitridation followed by deposition of a thin (<50 nm) low-temperature InN or GaN buffer layer. Although most of the samples were not intentionally doped, free electron concentrations ranging from 3.5×10^{17} to 5.5×10^{18} cm^{-3} have been found in samples of set I by Hall effect measurements. Samples in set I which were doped with Si had even higher free electron concentrations ranging from 1.0×10^{19} to 4.5×10^{19} cm^{-3}. All the samples in set II were not intentionally doped. Free electron concentrations ranging from 3.5×10^{19} to 4.5×10^{20} cm^{-3} were obtained by varying the residual H_2O and O_2 levels in the growth chamber.[7] X-ray diffraction studies have confirmed that all InN samples studied were wurtzite epitaxial layers with the orientation relationship InN(0001)//Al_2O_3(0001) or InN($11\bar{2}0$)//Al_2O_3($10\bar{1}0$). Hall mobilities range from ~600 up to 2000 cm^2/Vs for the samples of set I and from ~50 to 500 cm^2/Vs for the set II samples.

The optical absorption measurements were performed at room temperature using a CARY-2390 NIR-VIS-UV spectrophotometer. Secondary ion mass spectrometry (SIMS) experiments were performed using a Cameca IMS 6f magnetic sector instrument with cesium primary beam and detection of O^-, H^-, InN^- negative secondary ions. SIMS standard samples were prepared by implanting oxygen and hydrogen at controlled doses into a thick, undoped InN film ($n=3.5\times10^{17}$ cm^{-3}). The ion yield obtained from the standard sample was used to calibrate the O and H concentrations in other samples.

Figure 1 shows the absorption curves of four representative InN films. The two curves with lower absorption edges are from set I samples and the other two are from set II samples. In all cases, the absorption coefficient rises to above 5×10^4 cm^{-1} for a photon energy of ~0.5 eV above the absorption edge. The absorption edge energy or optical band gap, E_{abs}, was determined by extrapolating the linear part of the squared absorption curves down to the baseline. The op-

a)Electronic mail: w_walukiewicz@lbl.gov

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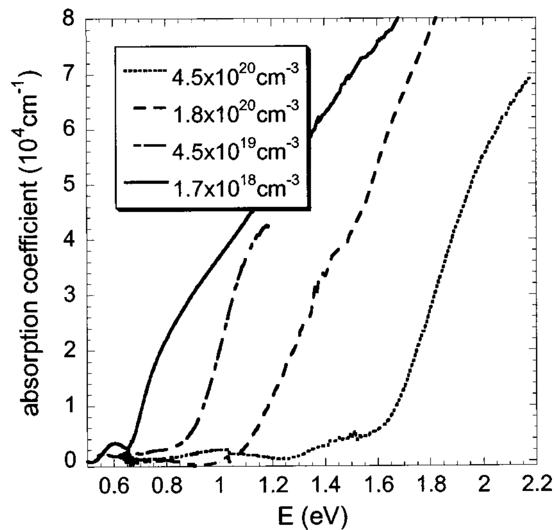

FIG. 1. Absorption spectra of InN films with different free electron concentrations.

tical band gaps obtained are plotted as a function of free electron concentration in Fig. 2. The error of the Hall effect measurements is less than 10%. Combining this with the uncertainties in determining the film thickness, we estimate the error of the electron concentration to be less than 20%.

A strong Burstein–Moss shift of the absorption edge with increasing carrier concentration can be clearly seen in Fig. 2. Interestingly, the two sets of data points that cover mostly different electron concentration ranges connect very well on the plot. The optical band gap varies continuously from ~0.7 eV, the intrinsic band gap of InN, to ~1.7 eV for the sample with 4.5×10^{20} cm^{-3} free electrons. This maximum value is close to the previously accepted value of the band gap of InN (~1.9 eV) obtained from sputter grown, degenerately doped InN films. Some previously reported data points adopted from the literature are also shown in Fig. 2.[8] Altogether, these data obtained from different sample sets show a consistent electron concentration dependence of the optical band gap.

In Ref. 5 we have shown that the lowest conduction

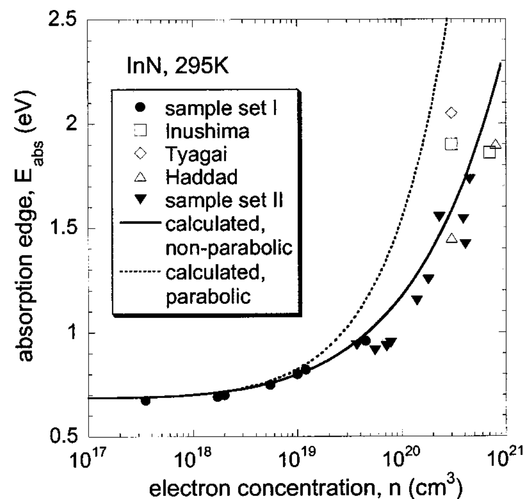

FIG. 2. Energy of optical absorption edge as a function of free electron concentration covering three decades of change. Some previous data points are also shown (Ref. 8). The solid curve shows the calculated optical absorption edge.

band of InN is highly nonparabolic due to the **k·p** interaction across the narrow direct gap between the conduction and valence bands. The nonparabolic dispersion relation for the conduction band has been obtained from Kane's two-band **k·p** model:[5]

$$E_C(k)=E_G+\frac{\hbar^2k^2}{2m_0}+\frac{1}{2}\left(\sqrt{E_G^2+4E_P\cdot\frac{\hbar^2k^2}{2m_0}}-E_G\right), \tag{1}$$

where $E_G\approx0.7$ eV is the intrinsic band-gap energy, and $E_P=2|\langle S|P_x|X\rangle|^2/m_0\approx10$ eV is an energy parameter related to the interaction momentum matrix element. Due to the Fermi exclusion principle, optical transitions can only occur for photon energies higher than the energy needed for electrons to make vertical transitions from the valence band up to the Fermi surface in the conduction band. The increase in Fermi energy with increasing electron concentration is given by the dispersion relation in Eq. (1) evaluated at the Fermi wave vector $k_F=(3\pi^2n)^{1/3}$. This approach assumes a strongly degenerate electron gas and neglects the thermal broadening of the Fermi distribution. We have calculated the absorption edge for a wide range of electron concentrations using this model. In the calculation we have also taken into account the conduction band renormalization effects due to the electron–electron interaction and the electron-ionized impurity interaction.[5] The results are in good agreement with the measured optical band gaps, as indicated by the solid curve in Fig. 2. The dashed curve is the calculated absorption edge energy assuming a parabolic conduction band, which shows a Burstein–Moss shift too fast to describe the experimental data.

It has been proposed that the large discrepancy between the previously measured large band gap of InN and the recently discovered narrow band gap could be due to the formation of indium oxynitride alloys in older sputter-grown films, since sputtered films often contain high levels of O contamination that can be over 10% in some extreme cases.[9] Assuming a linear composition dependence of the direct band gap of the alloy formed by InN and In_2O_3 [direct band gap ~3.2 eV (Ref. 10)] we find that the highest band gap of 1.7 eV observed in our samples would require an alloy with 40% In_2O_3, corresponding to an oxygen concentration above 10^{22} cm^{-3}. Clearly such high levels of O contamination are not expected in MBE grown InN and are highly unlikely even for sputtered samples.

To further elucidate the origin of band-gap variation, we have performed SIMS experiments on selected, *not intentionally doped* films. In addition to oxygen,[11] hydrogen[12,13] has also been suggested as a possible donor in InN. Considering the growth process, these two elements are the most likely candidates among possible donor contaminants. In the inset of Fig. 3, a set of SIMS curves obtained from a film with $n=5.5\times10^{19}$ cm^{-3} is shown. It can be seen that both the O and H concentrations are lower than the free electron concentration. The average concentration is obtained by integrating the concentration curve over the depth and dividing by the film thickness. In Fig. 3 the average O and H concentrations are compared with electron concentration for all measured samples. There is an overall trend of higher O and H concentration for the samples with larger free electron

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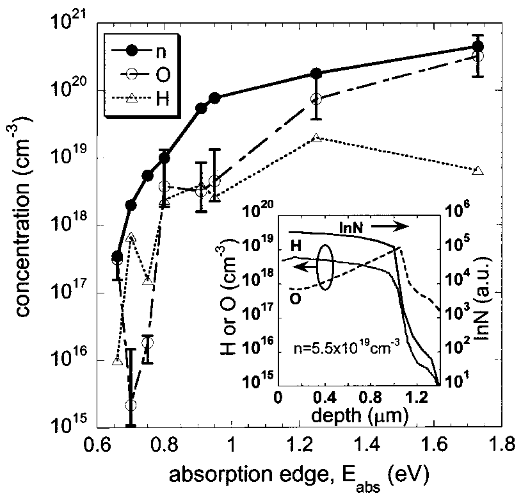

FIG. 3. Free electron concentration shown in comparison with oxygen and hydrogen concentrations. The inset shows the SIMS data of an InN film with $n = 5.5\times10^{19}$ cm^{-3}.

concentration. In fact, in the most heavily doped samples the O concentration is, within experimental error, equal to the electron concentration. However, it is also evident that in some instances the concentrations of O and/or H are too low to account for the electron concentration. This indicates that intrinsic defects such as N vacancies[11] and/or dislocations[14] could be important additional sources of free electrons in these samples. It is important to note that in all films, the O concentration is far too low to explain the increase in the band gap purely by InN–In_2O_3 alloying effect. Therefore, we can safely exclude alloying as the origin of the large optical band-gap variations in InN. We also note that in a recent paper[15] it was reported that the optical band gap of polycrystalline InN increases from ~1.6 to ~2.2 eV for oxygen concentrations ranging from 1% to 6%. Assuming that all the oxygen atoms are electrically active substitutional donors in those samples, their data points agree reasonably well with the calculated curve shown in Fig. 2.

Our study shows that the electron concentration can vary by orders of magnitude in nominally undoped MBE grown InN. This striking propensity for n-type doping can be attributed to the extremely large electron affinity of InN. The conduction band of InN is located at about 5.7 eV below the vacuum level or 0.8 eV below the Fermi level stabilization energy (E_{FS}) that represents the average energy of the dangling bonds in semiconductors.[16] The unusually low location of the conduction band edge strongly favors incorporation of donor impurities and formation of donor-like native defects. According to the amphoteric defect model,[17] the dangling bond defects have a donorlike character until the Fermi level reaches E_{FS}. At this point the formation energies of donor- and acceptor-like native defects become equal, resulting in a stabilization of the Fermi energy. This assertion has been recently confirmed by a study of free InN surfaces indicating that indeed the surface Fermi level pinning position is stabilized at about 0.8 above the conduction band edge.[18]

In conclusion, we have grown and characterized InN films with a wide range of electron concentrations. The optical absorption edge energy of these films strongly depends on the electron concentration and varies between 0.7 and 1.7 eV. The variation in the absorption edge can be fully explained by the effect of Fermi level increase as a result of free electron doping. An analysis of the SIMS results shows that oxygen and hydrogen doping cannot fully account for the free electron concentration, suggesting an important role of native defects. Also the results exclude the possibility that O alloying effects could explain the observed changes of the absorption edge energy.

After the completion of the manuscript, we noted a most recent paper by Bhuiyan *et al.* that relates the variation of absorption edge of InN to the Burstein–Moss effect.[19] Our work shows specifically the quantitative agreement between the Burstein–Moss effect and the experimental data over the full range of 0.7–2 eV. By SIMS experiments we also clarified the insufficient roles of O and H impurities as donors in InN.

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