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Butcher, K. S. A., Chen, P. P.-T. & Downes, J. E. (2012). Low activation energy for the removal of excess nitrogen in nitrogen rich indium nitride. *Applied physics letters*, 100(1), 011913 and may be found at [http://apl.aip.org/resource/1/applab/v100/i1/p011913\\_s1](http://apl.aip.org/resource/1/applab/v100/i1/p011913_s1)

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# Low activation energy for the removal of excess nitrogen in nitrogen rich indium nitride

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(Received 6 October 2011; accepted 9 December 2011; published online 6 January 2012)

For some InN films large amounts of excess nitrogen are seen at low growth temperatures. Recent studies have revised downward the defect formation energies for several forms of nitrogen rich point-defects in InN. Here we calculate an activation energy of  $0.4 \pm 0.1$  eV for the thermally activated removal of much of the excess nitrogen, believed to be interstitial nitrogen. This low energy barrier is shown to support the case for a low defect formation energy of the same native defect, although it is pointed out that non-equilibrium plasma based conditions are required to reach these lower defect formation energies. © 2012 American Institute of Physics. [doi:10.1063/1.3673839]

For indium nitride it had long been assumed, mainly on the basis of early theoretical papers, that the primary native defect in InN would be the nitrogen vacancy<sup>1-3</sup> and that nitrogen rich native defects could not exist in significant densities.<sup>2,3</sup> However, as early as 2002 (Ref. 4) and more widely afterward,<sup>5-13</sup> we published work on the observation of surprisingly large amounts of excess nitrogen measured in InN grown by RF sputtering, remote plasma enhanced chemical vapour deposition (RPECVD), and to a lesser extent, in some thin plasma assisted molecular-beam epitaxy (PA-MBE) grown samples. In some extreme cases, for films grown at low temperatures, we measured N/In ratios as high as 1.7.<sup>10</sup> Since that time at least 6 other groups have independently observed experimental evidence of nitrogen rich defects in InN.<sup>14-20</sup>

The physical existence of nitrogen rich InN has therefore been well tested experimentally. However, until quite recently a theoretical basis for the existence of such defects and at extremely high densities has been missing. Theoretical calculations, of course, assume conditions of thermodynamic equilibrium, which may not be present for many actual film growth experiments, however, may still be hoped that accurate calculations can act as a guideline as to what defects might be expected in real experimental situations. Earlier calculations by Stampfl *et al.*<sup>2</sup> on zincblende InN grown under indium rich conditions have been assumed to also be valid for wurtzite InN. In 2009, however, Duan and Stampfl<sup>21</sup> published their calculations for the formation energies of native defects for “wurtzite” InN. They found that there were significant differences between the wurtzite case and the older zincblende data published in 2000 and that it was important to also consider nitrogen rich growth conditions. In particular, Duan and Stampfl have found that the formation energy for nitrogen interstitials is not  $\sim 6$  eV in wurtzite material, as assumed from the 2000 paper, but may fall to very low values, to less than 1 eV under some predicted growth conditions; that is, to energies that, under certain growth conditions, would allow it to be the dominant

native defect for InN. These calculated formation energies for wurtzite InN have also been independently corroborated by another group who have published similar values for wurtzite InN native defects.<sup>22</sup>

We have grown a number of samples using RPECVD at different temperatures. The growth conditions have been reported elsewhere;<sup>10</sup> however, the main point to keep in mind here is that the RPECVD film growth was carried out using a remote nitrogen plasma that predominantly makes use of neutral excited molecular nitrogen species, in particular the  $N_2^*(A^3\Sigma_u^+)$  species, as the nitrogen precursor. These samples were all found to be nitrogen rich, some of them extremely so. Keeping in mind the pitfalls of many standard chemical analysis techniques when applied to InN (see the review by Butcher and Tansley<sup>23</sup>) we applied a stoichiometry analysis technique whose methodology has been developed specifically for accurate In:N determination, that is elastic recoil detection (ERD) analysis.<sup>6,8,11</sup> Figure 1 shows

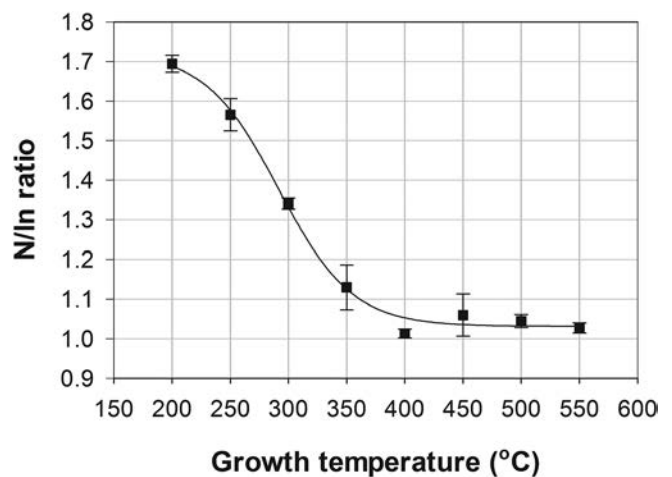


FIG. 1. N/In data for RPECVD grown InN at different film growth temperatures. Note that the temperatures presented are substrate temperatures only and that a small additional systematic error arises in our calculation of the activation energy because of the difference in temperature between the substrate holder and the top surface of the substrate. Unfortunately it is impractical to measure the temperature of the substrate surface with greater accuracy.

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the N/In ratios, reported previously in reference,<sup>10</sup> which were measured for the films as a function of film growth temperature. As shown in the plot the N/In ratio is very high for the film growth temperature of 200 °C but drops steadily to only slightly nitrogen rich stoichiometry at film growth temperatures of 400 °C and greater.

Nitrogen loss in InN films has been noted during heavy ion bombardment to follow the bulk molecular recombination model.<sup>7</sup> Data fitting with that model has indicated the importance of the diffusion of nitrogen species with the subsequent recombination of nitrogen radicals into N<sub>2</sub>. Although differences are expected in the absence of heavy ion bombardment, for the films grown here the nitrogen loss for the samples grown at higher temperatures (as evidenced by Fig. 1) is certainly a thermal process with some similarity to the results seen for InN under heavy ion bombardment. In particular, the process for the removal of the N<sub>i</sub> species is likely to involve a two step process, including diffusion of the interstitial species from the lattice and the subsequent formation of a species that is easily lost from the lattice surface, i.e., an N<sub>2</sub> molecule. The main mechanism that limits the rate of N<sub>i</sub> loss—diffusion or recombination into N<sub>2</sub>—cannot be distinguished with our present data. However, for a simple first order analysis both processes are thermally activated and can be described by an Arrhenius type relationship. In the case of diffusion, the diffusion coefficient (D) is given by the standard relationship

$$D = Ae^{-E_A/RT}, \quad (1)$$

where A is the frequency factor, R is the gas constant, T is temperature, and E<sub>A</sub> is the activation energy of diffusion from one lattice site to the next (given per mole in the equation). Similarly, for a chemical reaction involving the recombination of two N<sub>i</sub> atoms into molecular nitrogen the reaction rate constant (k) is given by

$$k = Ae^{-E_A/RT}, \quad (2)$$

where for this case A is related to the frequency of reacting atoms crossing the reaction barrier and E<sub>A</sub> is the activation energy of the reaction. The limiting mechanism for the nitrogen loss process will therefore be the mechanism with the higher activation energy. To determine this dominant activation energy for the process we do not need a thorough knowledge of the absolute values of either k or D as the activation energy is determined from the slope of a natural log plot of k (or D) versus 1/T. To obtain an accurate slope we only require data that is proportional to D and/or k. In this case the value of the excess nitrogen present in the films (N/In-1) at the end of film growth will suffice, as the film growth period for each of the films in Fig. 1 is constant at 10 h. The activation energy can therefore be calculated from the slope of Fig. 2, and we find that this value is equal to 0.4 ± 0.1 eV. Unfortunately the use of values proportional to k (or D) and our lack of knowledge regarding the exact mechanism which limits the nitrogen loss prevents any further thermal data (such as Gibbs free energy) from being extracted from this plot. Furthermore, we have not determined the exact value of the activation energy for the chemical reaction to molecular

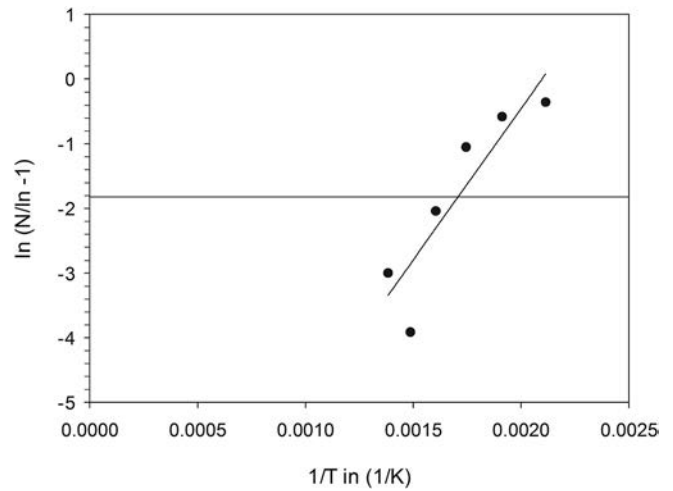


FIG. 2. Arrhenius plot derived from the data of Fig. 1. The error in the activation energy is taken from the standard deviation of the points on the graph.

nitrogen; however, as we have calculated the dominant energy of the process, we can say that this energy is  $\leq 0.4 \pm 0.1$  eV.

This activation energy is extremely low and suggests a quasi stable system. Duan and Stampfl<sup>21</sup> have suggested that the 2- and 3- charge states for the N<sub>i</sub> defect are unstable in InN. Given the high electron carrier concentrations of the samples examined ( $>10^{19}$  cm<sup>-3</sup>) the presence of extra electrons in the lattice would promote an unstable bonding configuration and could promote interstitial hopping of the N<sub>i</sub> species.

The low activation energy of this process also suggests that the reverse process for the formation of N<sub>i</sub> is not a high energy process with formation energy of almost 6 eV as suggested by the 2000 paper of Stampfl *et al.*<sup>2</sup>; otherwise, the defect would anneal out much quicker than it was formed and would not be present at any appreciable concentration. However, even the lower formation energies of Duan and Stampfl<sup>21</sup> at values of  $\sim 2.3$ - $2.9$  eV, for material grown under N-rich conditions with a high Fermi level, seem too high to allow appreciable amounts of nitrogen interstitial to accumulate. It should be noted, however, that the formation energy calculations for the native defects of InN explicitly assume conditions of thermodynamic equilibrium. This is clearly stated in those papers for which the calculations have been performed.<sup>2,21</sup> However, the solution to the presence of the high levels of the N<sub>i</sub> that have accumulated during growth can be understood when it is realised that plasma based film growth is not carried out under conditions of thermodynamic equilibrium. In fact most InN films grown in recent times have not been grown under such conditions. InN has predominantly been grown by plasma based methods, such as PA-MBE. Plasma based film growth techniques are inherently non-equilibrium growth techniques. For instance, for the films grown for this study, using remote plasma based film growth, the lowest energy excited neutral nitrogen molecular species was the predominant nitrogen precursor used. This N<sub>2</sub><sup>\*</sup> (A<sup>3</sup>Σ<sub>u</sub><sup>+</sup>) species has a potential energy of approximately 6.1 eV.<sup>24</sup> The heat of formation for InN, given by Duan and Stampfl,<sup>21</sup> is approximately 1.2 eV. Because of

quantum considerations a nitrogen molecule excited to the  $N_2^*(A^3\Sigma_u^+)$  state must lose all its potential energy to participate in the formation of an InN molecule. This means that a minimum of  $6.1-1.2\text{ eV}=4.9\text{ eV}$  of excess energy (and an extra nitrogen atom) is available for defect formation when using this excited species for film growth. This excess energy is insufficient to reach the  $\sim 6.0\text{ eV}$  formation energy for  $N_i$  given by Stampfl *et al.*<sup>2</sup> but is more than sufficient to overcome the formation energies provided for the same defect by Duan and Stampfl under all the conditions they provide (N-rich and In-rich).<sup>21</sup> It is therefore not surprising that large amounts of excess nitrogen accumulate in InN at low growth temperatures when using plasma based growth systems, since the defect formation energy is essentially overcome by the  $\sim 4.9\text{ eV}$  excess energy available from the plasma precursor species. The availability of the excess energy provided by plasma species also explains the high levels of indium vacancies that have been observed with positron annihilation spectroscopy for PA-MBE grown InN films.<sup>20</sup> It has been noted that these defects are present in that material at much higher concentrations than are expected for thermodynamic equilibrium growth conditions.<sup>20</sup> However, again, the  $\sim 4.9\text{ eV}$  excess energy of the plasma species available after interacting to form InN is sufficient to reach the formation energy of that defect under many growth conditions. It should be noted that for the slight nitrogen rich stoichiometry of our samples grown at temperatures above  $400^\circ\text{C}$  (Fig. 1) there appears to be a more temperature resilient residual nitrogen rich defect, or defects, present that may include indium vacancies. In the RPECVD case, the  $N_2^*(A^3\Sigma_u^+)$  plasma species used would provide enough excess energy to form those species under some growth conditions.

It should be pointed out that for material grown using RF sputtering and other direct plasma techniques, defects with even higher formation energies may also be present because much higher energy plasma species are generated under such environments. Hence, the film growth is much further away from conditions of thermodynamic equilibrium. However, low growth temperatures may be required to maintain the presence of such defects, as defect removal activation energies, as in the case of the nitrogen interstitial, may be low enough for their removal at elevated growth temperatures. Post-growth annealing may also be useful in this respect.

Finally, we conclude that the existence of nitrogen rich native defects in InN is now a well established phenomenon, with sound experimental and theoretical foundations. The p-type indium vacancy, observed directly by positron annihilation spectroscopy,<sup>20</sup> is one example and explains the background compensation of n-type material by low levels of p-type carriers observed in Hall effect experiments of PA-MBE samples.<sup>25</sup> Similarly the electrical role of the nitrogen interstitial can be speculated upon. Duan and Stampfl have suggested the presence of a split interstitial which induces defect states in the conduction band and may therefore be electrically active. Whether the largely unstable defects addressed here are split interstitials or otherwise is not clear at the moment, however they are highly mobile and may therefore diffuse even at room temperature to defect areas, such as the InN surface, where they become trapped. At such

surfaces they may contribute to the electron concentration through dangling bonds if unable to combine with other interstitials and form  $N_2$  molecules. It is to be noted that in a previous XPS study we identified a species—most abundant for very nitrogen rich InN, but present at the surfaces of many samples in percentage amounts—which appears to be a nitrogen interstitial species.<sup>13</sup> The observation of this highly mobile, quite probably electrically active, nitrogen rich native defect at the surface of InN suggests that we have positively identified a defect species that contributes to the surface electron accumulation effect observed for InN, and it is possible too that this defect may have a role in the bulk conductivity of some InN samples, especially those grown far from thermodynamic equilibrium conditions.

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Citation: *Appl. Phys. Lett.* **100**, 011913 (2012); doi: 10.1063/1.3673839

View online: <http://dx.doi.org/10.1063/1.3673839>

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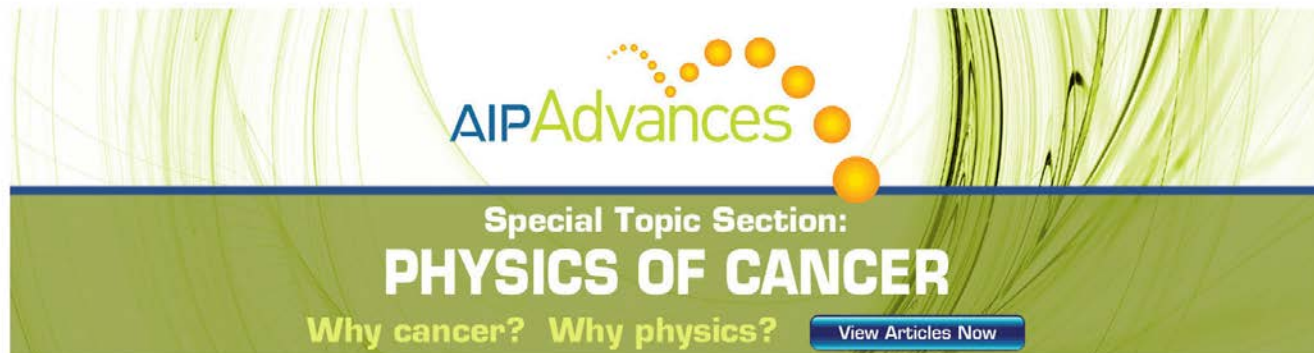
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Start Year: 1962

Frequency: Weekly

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