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Undoped p -type $\text{GaN}_{1-x}\text{Sb}_x$ alloys: Effects of annealing

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We report p -type behavior for undoped $\text{GaN}_{1-x}\text{Sb}_x$ alloys with $x \geq 0.06$ grown by molecular beam epitaxy at low temperatures ($\leq 400^\circ\text{C}$). Rapid thermal annealing of the $\text{GaN}_{1-x}\text{Sb}_x$ films at temperatures $> 400^\circ\text{C}$ is shown to generate hole concentrations greater than 10^{19} cm^{-3} , an order of magnitude higher than typical p -type GaN achieved by Mg doping. The p -type conductivity is attributed to a large upward shift of the valence band edge resulting from the band anticrossing interaction between localized Sb levels and extended states of the host matrix.

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Gallium nitride is a well-established material for applications in light-emitting diodes (LEDs), laser diodes (LDs), and high power, high frequency electronic devices (see e.g., Refs. 1 and 2). Bipolar p - and n -type doping is essential for optoelectronic applications of any semiconductor material. However, GaN is intrinsically n -type, and p -type doping has been difficult to achieve. This behavior has been attributed to the very low location of the valence band edge (VBE) at 7.5 eV below the vacuum level.³ The p -type doping problem has been solved in seminal works of Japanese scientists. Amano *et al.*⁴ showed that highly resistive Mg-doped GaN grown by metal-organic chemical vapor deposition (MOCVD) became p -type when irradiated with a low-energy electron beam. Later, Nakamura *et al.*⁵ obtained p -type GaN by thermal annealing of the Mg-doped layers at 700°C under a N_2 ambient. These breakthroughs paved the road to a much broader range of practical applications of group III-nitride semiconductors. Although p -doping can now be regularly accomplished, increasing the range of achievable p -type conductivity is highly desirable for improved device performance. To date, the highest reported values on the hole concentration of Mg-doped GaN layers range from high- 10^{17} to low- 10^{18} cm^{-3} with corresponding resistivities ranging from 5 to $0.5\ \Omega\text{ cm}$.^{6,7} It is now well established that the high ionization energy of Mg acceptors^{8,9} and the compensation by native donor-like defects are responsible for the low hole concentration.^{10–12}

Recently, a study of GaN grown by low temperature molecular beam epitaxy (LT-MBE) at 80°C reported that thin films grown under N-rich conditions were insulating whereas the samples grown under Ga-rich conditions were conductive with a resistivity in the range of 10^{-1} – $10^{-3}\ \Omega\text{ cm}$.¹³ A positive Seebeck coefficient was measured for the Ga-rich samples indicating that the samples were p -type. The p -type conductivity was attributed to a high concentration of gallium antisite defects forming a partially filled band in the bandgap. Similar results were obtained in our recent study of $\text{GaN}_{1-x}\text{Sb}_x$

thin films grown at a low temperature of 325°C where we found that alloys with higher Sb contents exhibit p -type conductivity.¹⁴

A modest amount of studies on the effect of annealing polycrystalline GaN and its alloys have been conducted.^{15–19} Recent studies indicate that annealing improves the structural and optical properties of polycrystalline GaN layers by re-crystallizing the GaN grains. For polycrystalline InGaN thin films, rapid thermal annealing (RTA) experiments found the crystallinity to be improved by annealing and the resistivity to be reduced by two orders of magnitude due to the annealing-induced increase in the carrier concentration.¹⁹ However, there are no thorough studies of the effects of thermal annealing on the electrical properties of polycrystalline GaN.

In this letter, we study the effect of rapid thermal annealing on the electrical and structural properties of $\text{GaN}_{1-x}\text{Sb}_x$ films. The films were grown by plasma-assisted molecular beam epitaxy (PA-MBE) at temperatures 325 and 400°C . We show that proper thermal annealing stabilizes the p -type conductivity of undoped $\text{GaN}_{1-x}\text{Sb}_x$ with $x \geq 0.06$. The effect is explained by the rapid, Sb-induced upward shift of the valence band edge. The analysis of the electronic band structure and the location of the Fermi level of these alloys on the absolute scale suggest that the alloys could serve as energy selective hole emitters.

The samples were grown in a GENII MBE system with a Veeco Uni-bulb plasma source to provide active N, elemental Ga, and a Veeco valved cracker-source for Sb. All films were grown on uncoated sapphire substrates, with the temperature set by the thermocouple. The Ga cell was set to a temperature corresponding to a GaN growth rate on sapphire of $0.10\ \mu\text{m/h}$ and a GaSb growth rate on GaSb of $0.25\ \mu\text{m/h}$. Two sets of $\text{GaN}_{1-x}\text{Sb}_x$ thin films are studied in this letter. The first set consists of the previously reported films^{14,20} grown by multilayer intermixing at a constant temperature of 325°C with an Sb composition x up to 0.30 along

FIG. 1. XRD patterns of as-grown $\text{GaN}_{1-x}\text{Sb}_x$ films.

with a film grown by the same method but at a slightly higher temperature of 400 °C with $x = 0.56$. The second set of $\text{GaN}_{1-x}\text{Sb}_x$ films was grown conventionally as a bulk alloy without any modulation of the Sb or N shutters, and consisted of two samples grown using LT-MBE at temperatures of 400 °C resulting in Sb contents $x = 0.27$ and 0.30. The layer thicknesses are in the range 150 to 300 nm for the first set and 220 to 320 nm for the second set. The composition and the thickness of the films were determined using Rutherford Backscattering Spectrometry (RBS). The RBS data did not show any compositional non-uniformity for any of the samples.

Transmission electron microscopy (TEM) measurements performed on selected samples of the first set were reported in Ref. 20. The TEM results showed that GaN grown without Sb is polycrystalline with grains primarily

consisting of 2H GaN with the (0002) planes aligned with the (0006) sapphire substrate planes. The grains were found to be randomly oriented in-plane. The structure of the thin film with $x = 0.06$ consisted of randomly oriented grains. The TEM results for the films with $x = 0.18$ and 0.42 showed an amorphous matrix with small crystalline grains. Some Sb segregation could be seen for the film with $x = 0.42$. No sign of the presence of any nanometer size secondary phase clusters was seen in the TEM results. More details of the crystal growth, characterization, and optical properties of the samples grown at 325 °C are presented in Refs. 14 and 20.

The structural properties of the $\text{GaN}_{1-x}\text{Sb}_x$ thin films were further studied using x-ray diffraction (XRD). A Siemen's D500 diffractometer in the Bragg-Brentano geometry with a Cu K α source was used for this purpose. Figure 1 shows $2\theta-\omega$ scans over a 2θ range of 20°–60° for the as-grown $\text{GaN}_{1-x}\text{Sb}_x$ films. The GaN sample grown without Sb shows the typical XRD peak at $2\theta \sim 34.4^\circ$ associated with the (0002) diffraction of hexagonal GaN with a strong preferential c -axis orientation along the growth direction. We note that the GaN (0002) peak is observed for all the samples since this diffraction peak comes primarily from a thin epitaxial GaN buffer layer (~ 26 nm) grown on the sapphire prior to the growth of the $\text{GaN}_{1-x}\text{Sb}_x$ films. As shown in Fig. 1, additional peaks at lower and higher angles appear in the XRD patterns for samples with high Sb contents ($x \geq 0.18$). These peaks are attributed to the (111), (200), and (311) diffraction of zinc blende GaSb indicating the presence of phase separated GaSb clusters within the $\text{GaN}_{1-x}\text{Sb}_x$ thin film.

Rapid thermal annealing was performed on the $\text{GaN}_{1-x}\text{Sb}_x$ films using a sealed ULVAC MILA 3000 RTA furnace. The annealing temperature ranging from 450 to 750 °C was varied with a temperature increment of 50 °C. The cumulative annealing was performed under an atmospheric

FIG. 2. XRD patterns of $\text{GaN}_{1-x}\text{Sb}_x$ films RTA at 550 and 650 °C with an Sb content of (a) 18%, (b) 30%, (c) 42%, and (d) 56% compared to the as-grown films.

FIG. 3. TEM results for the annealed sample with 18% Sb showing (a) GaSb clusters and (b) a large GaSb cluster surrounded by GaN crystallites and amorphous GaNSb.

pressure N_2 ambient for 30 s. A visual degradation of the surface of the samples could be observed for the annealing temperatures higher than 650°C . The degradation could be related to the dissociation pressure of GaN increasing after 700°C .²¹

Figure 2 shows a comparison between the XRD patterns of as-grown and annealed films covering a 2θ range of 31.8° – 37.5° . As the annealing temperature increased from 550 to 650°C , a peak at $2\theta \sim 32.6^\circ$ becomes more prominent, particularly for the films with higher Sb contents of 42% and 56%. This peak corresponds to a d -spacing of roughly $2.7 \text{ \AA}$. Although the TEM data does show small GaSb grains for these films, there are no planes within these grains that

correspond to this XRD peak. The peak corresponds to the m -plane of GaN, which is seen in the diffraction patterns in TEM samples for annealed films having Sb contents at or exceeding 18%. GaN crystallites having the m -plane oriented along the growth direction were observed in the high resolution images of these samples. The samples grown with the interlayer mixing technique had less preferred orientation along the growth direction, with grains much more randomly oriented than in the conventionally grown GaNSb alloys. If the Sb containing regions have segregated in the higher Sb-containing films, it may follow that there are regions consisting of pure GaN in the matrix phase. Therefore, it would not be surprising to see other orientations of GaN besides the (0002) direction that was seen in the bulk alloys which had preferentially aligned with the substrate. Figure 3 shows TEM results for the sample with 18% Sb obtained after cumulatively annealing the film to a temperature of 650°C . In Fig. 3(a), GaSb clusters are highlighted with circles, and are surrounded by polycrystalline and amorphous GaN and GaNSb. The separation and size of these clusters are not meant to illustrate an average. The clusters are of various size and separation throughout the film. Figure 3(b) shows a large GaSb cluster surrounded by GaN crystallites and amorphous GaNSb material. Representative GaN planes are denoted by label 1, GaSb by label 2, and the poly-amorphous matrix by label 3.

The measured resistivity and Seebeck coefficient for the RTA $\text{GaN}_{1-x}\text{Sb}_x$ films are shown in Fig. 4. The samples with lower Sb or no Sb contents were too resistive to be measured. The positive thermopower indicates p -type conductivity for all measured samples. In general, the annealing results show a decreasing resistivity with a decreasing Seebeck coefficient for the films. The resistivity of the films seem to converge towards similar values between 0.2 and $2 \Omega\text{cm}$ when the annealing temperature reaches 600°C .

Hall effect measurements of the RTA $\text{GaN}_{1-x}\text{Sb}_x$ films are presented in Fig. 5. The carrier concentration and mobility could not be reliably determined for samples with the

FIG. 4. The measured (a) resistivity and (b) Seebeck coefficient for RTA $\text{GaN}_{1-x}\text{Sb}_x$ films.

FIG. 5. The measured hole concentration for RTA $\text{GaN}_{1-x}\text{Sb}_x$ films. The inset shows the corresponding hole mobility of the alloys.

lowest Sb contents. Also, for the samples with $x = 0.18$ and 0.42 grown by the multilayer intermixing method, measurements could only be carried out after annealing at 500 and 550°C , respectively.

The measured positive sign of the Hall coefficient confirms that the $\text{GaN}_{1-x}\text{Sb}_x$ thin films with higher Sb contents are p -type. The hole concentration for the as-grown samples with 27, 30, and 56% Sb is determined to be $\sim 2 \times 10^{18} \text{ cm}^{-3}$, a value already comparable to the highest reported values on the hole concentration for Mg-doped GaN films.^{6,7} Annealing tends to further increase the hole concentration; however, the mobility remains almost unchanged. The highest values of the hole concentration and corresponding lowest resistivities are reached after annealing the films at temperatures of 550 to 600°C . The highest hole concentration of $1.3 \times 10^{19} \text{ cm}^{-3}$ is measured for the film with an Sb content of 30% after RTA at 600°C . The corresponding mobility and resistivity of the sample are $\sim 1 \text{ cm}^2(\text{Vs})^{-1}$ and $0.43 \Omega \text{ cm}$, respectively. This is a clear improvement compared to Mg-doped GaN films for which the corresponding highest values of the hole concentration are in the low- 10^{18} cm^{-3} .

There are two possible reasons for the p -type conductivity of the GaNSb alloys. The alloys could separate into GaSb and GaN phases with the p -type conductivity originating from the GaSb phase forming an electrically connected network. This is a highly unlikely scenario as the thermopower measurements shown in Fig. 4 indicate that p -type conductivity is observed in the samples with only 6% of Sb in which the presence of connected, electrically conducting GaSb phase in the dominant GaN phase is impossible. No GaSb (or Sb) clusters are observed in as-grown samples with $x < 0.42$. For annealed samples with $x \geq 0.18$, TEM and XRD reveal that some isolated GaSb clusters with diameters of $\sim 3 \text{ nm}$ are embedded in GaNSb matrix as shown in Figs. 3(a) and 3(b). Therefore, it is reasonable to assume that the phase separation mechanism is not responsible for the p -type conductivity in most of the as-grown and annealed GaNSb samples.

A more viable explanation for the p -type conductivity can be offered by considering the changes in the electronic

band structure of the GaNSb alloys based on a modified band anticrossing (BAC) model.¹⁴ According to the model, the large reduction of the bandgap of GaNSb alloys is due to an abrupt upward shift of the VBE at low Sb content. The inset of Fig. 6 shows the calculated density of states (DOS) of $\text{GaN}_{1-x}\text{Sb}_x$ for $x = 0, 0.05$, and 0.3 using the modified BAC model. Partial replacement of N with Sb in GaN produces an additional band with large density of states well above the VBE of GaN. This fully occupied, Sb-derived band forms a new VBE that is located more than 1 eV above the VBE of GaN. In contrast, incorporation of Sb has only a minor effect on the electronic structure of the conduction band.

The large upward shift of the VBE DOS has a profound effect on the charge carriers of GaNSb alloys. According to the amphoteric defect model,^{22,23} the nature of the dominant native defects and the doping behavior of semiconductor materials are determined by the location of the band edges relative to the common energy reference, the Fermi level stabilization energy (E_{FS}) located at 4.9 eV below the vacuum level. Thus, semiconductors with a large density of the conduction (valence) band states closer to the E_{FS} show propensity for n -type (p -type) conductivity. This is well illustrated by the case of GaN which, as illustrated the inset of Fig. 6, has the VBE located about 2.5 eV below the E_{FS} whereas the conduction band edge (CBE) lies less than 1 eV above the E_{FS} . This is consistent with the well-known propensity of undoped GaN for n -type conductivity and difficulty in doping it p -type.

The calculations presented in the inset of Fig. 6 show that adding Sb to GaN to form $\text{GaN}_{1-x}\text{Sb}_x$ results in a drastic shift of the VBE. Thus, as is shown in the inset of Fig. 6 for $x = 0.3$, a large valence band DOS is located less than 1 eV below E_{FS} . This is expected to greatly affect the charge carriers in the alloys. To better evaluate the effect of the change in the electronic structure on the electrical properties, we have calculated the intrinsic Fermi level ($E_{\text{F,int}}$) in undoped

FIG. 6. Calculated (1) Fermi level of experimental samples annealed at 650°C based on the hole concentration at RT measured by Hall effect, and the BAC model; (2) Theoretical intrinsic Fermi level of $\text{GaN}_{1-x}\text{Sb}_x$ relative to the CBE, and VBE and E_{FS} of the alloy. The inset shows the calculated DOS of $\text{GaN}_{1-x}\text{Sb}_x$ with an Sb content of (a) 0%, (b) 5%, and (c) 30%.

GaN_{1-x}Sb_x at room temperature (RT) as a function of composition. The results in Fig. 6 show that the $E_{F,int}$, which is located well below the E_{FS} in GaN, moves up with composition and comes close to the E_{FS} for $x > 0.05$. The low location of $E_{F,int} \ll E_{FS}$ in GaN means that donor-like defects have a lower formation energy and are predominantly incorporated in this material. However, adding more Sb moves $E_{F,int}$ close to E_{FS} indicating that GaN_{1-x}Sb_x alloys with $x > 0.05$ have no clear preference for either *n*- or *p*-type behavior and the type of conductivity could be related to differences in defect reactions upon cooling of the non-stoichiometric material.

Figure 6 also shows the Fermi level calculated for the RT hole concentration determined from the Hall effect measurements of samples annealed at 650 °C. As can be seen, the Fermi level follows closely the VBE of the alloys. It means that GaN_{1-x}Sb_x alloys have a narrow partially occupied band lying as low as 6 eV below the vacuum level. This brings up an interesting opportunity of using GaN_{1-x}Sb_x alloys as hole emitters or energy selective contacts in photovoltaic devices as the upper VBE subband of the alloy with ~10% Sb lies close to the VBEs of many standard group III–V and group II–VI compound semiconductors.

In conclusion, using two different methods we have synthesized undoped, *p*-type GaN_{1-x}Sb_x alloys. We show that a proper rapid thermal annealing can produce thin films with hole concentrations higher than 10¹⁹ cm⁻³. The *p*-type conductivity is attributed to a large upward shift of the valence band edge resulting from the band anticrossing interaction between the localized Sb levels and extended states of the host matrix.

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- ¹H. Morkoc, *Nitride Semiconductors and Devices* (Springer Science & Business Media, 2013), Vol. 32.
- ²*Semiconductor Science and Technology: Gallium nitride electronics*, edited by S. Rajan and D. Jena (IOP Publishing, 2013), Vol. 28.
- ³W. Walukiewicz, *Phys. B: Condens. Matter* **302**, 123 (2001).
- ⁴H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, *Jpn. J. Appl. Phys., Part 2* **28**, L2112 (1989).
- ⁵S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys., Part 1* **31**, 1258 (1992).
- ⁶E. C. Kyle, S. W. Kaun, E. C. Young, and J. S. Speck, *Appl. Phys. Lett.* **106**, 222103 (2015).
- ⁷C. A. Humi, J. R. Lang, P. G. Burke, and J. S. Speck, *Appl. Phys. Lett.* **101**, 102106 (2012).
- ⁸W. Götz, N. Johnson, J. Walker, D. Bour, and R. Street, *Appl. Phys. Lett.* **68**, 667 (1996).
- ⁹R. J. Molnar and T. D. Moustakas, *Bull. Am. Phys. Soc.* **38**, 445 (1993).
- ¹⁰U. Kaufmann, M. Kunzer, H. Obloh, M. Maier, C. Manz, A. Ramakrishnan, and B. Santic, *Phys. Rev. B* **59**, 5561 (1999).
- ¹¹M. A. Reshchikov, G.-C. Yi, and B. Wessels, *Phys. Rev. B* **59**, 13176 (1999).
- ¹²P. Vennegues, M. Benaissa, S. Dalmaso, M. Leroux, E. Feltin, P. De Mierry, B. Beaumont, B. Damilano, N. Grandjean, and P. Gibart, *Mater. Sci. Eng., B* **93**, 224 (2002).
- ¹³K. Yu, M. Ting, S. Novikov, C. Collin, W. Sarney, S. Svensson, A. Luce, J. Denlinger, W. Walukiewicz, and C. Foxon, *J. Phys. D: Appl. Phys.* **48**, 385101 (2015).
- ¹⁴N. Segercrantz, K. M. Yu, M. Ting, W. L. Sarney, S. P. Svensson, S. V. Novikov, C. T. Foxon, and W. Walukiewicz, *Appl. Phys. Lett.* **107**, 142104 (2015).
- ¹⁵Z. Zhang, X. Pan, T. Wang, L. Jia, L. Liu, W. Wang, and E. Xie, *J. Electron. Mater.* **37**, 1049 (2008).
- ¹⁶D.-J. Kim, S.-E. Park, H.-J. Kim, J.-K. Ryu, O. Byung-sung, and S.-S. Pak, *Jpn. J. Appl. Phys., Part 1* **42**, 7349 (2003).
- ¹⁷A. Ariff, N. Zainal, and Z. Hassan, *Superlattices Microstruct.* **97**, 193 (2016).
- ¹⁸M. Samsudin, N. Zainal, and Z. Hassan, *J. Alloys Compd.* **690**, 397 (2017).
- ¹⁹S. Kazazis, E. Papadomanolaki, M. Androulidaki, K. Tsagaraki, A. Kostopoulos, E. Aperathitis, and E. Iliopoulos, *Thin Solid Films* **611**, 46 (2016).
- ²⁰W. L. Sarney, S. P. Svensson, M. Ting, N. Segercrantz, W. Walukiewicz, K. M. Yu, R. W. Martin, S. Novikov, and C. T. Foxon, *Appl. Opt.* **56**, B64 (2017).
- ²¹C. Thurmond and R. Logan, *J. Electrochem. Soc.* **119**, 622 (1972).
- ²²W. Walukiewicz, *Appl. Phys. Lett.* **54**, 2094 (1989).
- ²³W. Walukiewicz, *J. Vac. Sci. Technol. B* **5**, 1062 (1987).