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Reduced surface electron accumulation at InN films by ozone induced oxidation

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A room temperature ozone induced oxidation of thin InN films is proposed to improve the electric transport properties. The sheet carrier density is reduced upon oxidation by a value which is in the order of the electron concentration of an untreated InN surface. Thus, ozone effectively passivates the surface defect states on InN and might be an effective method to prepare InN films for electronic applications. A model for the improved electron transport properties is proposed taking into account the decreased surface band bending and the decreased influence of surface electrons on the net mobility of InN layers. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2721365]

Due to the very high predicted electron mobility[1] of $\mu \sim 12\,000\ \mathrm{cm^2/V\,s}$, indium nitride is a very promising low band gap semiconductor for high frequency devices. However, the high electron concentration $n > 10^{17}\ \mathrm{cm^{-3}}$ of InN layers prevents the development of any kind of electronic device despite of the remarkable progress in the growth of InN by different techniques such as plasma-induced molecular-beam epitaxy[2,3] (MBE) and metal-organic chemical vapor deposition.[4]

Generally, the electron concentration n decreases with increasing thickness th, and previously[5,6] it has been shown that at least three major mechanisms contribute to the apparent electron concentration: (1) a localized electron accumulation with specific sheet carrier concentration $N_{S,0}$ at the surface and the interface, (2) a homogeneous background volume concentration n_b, and (3) an inhomogeneous carrier distribution n_{inhom} over the InN film, which is mainly determined by dislocations inside the film.

While the bulk concentrations n_b and n_{inhom} are the subject of optimization of the epitaxial growth, the surface accumulation appears to be an intrinsic property of a clean InN surface as a result of the extraordinarily low conduction band at the Γ point, which allows donor-type surface states to be located inside the conduction band.[7] Recently it was proposed based on first principle calculations[8] that an In double layer is responsible for this phenomenon. However, we have shown that a partially oxidized InN (Refs. 9 and 10) surface after exposure to air has a very similar electron accumulation as *in vacuo* prepared samples.[7,11] Moreover, *in situ* deposited AlN (Ref. 12) or GaN (Ref. 13) top layers did not completely passivate the InN surface or interface, probably due to a high dislocation density. Thus, mechanisms for a complete passivation of the InN surface are highly recommended to reduce the surface accumulation. This could be achieved by a chemical modification of the surface, which passivates all the dangling bonds, for example, by sulfurization[14] or oxidation.

Recently, cubic In_2O_3 was proposed to grow layer by layer on InN by annealing at 550 °C.[15] Electrical properties were not investigated in this study; however, our oxidation experiments between 200 and 600 °C lead to an increasing rather than decreasing electron density, indicating the creation of additional defects upon annealing. A low temperature oxidation of the surface is expected to passivate the InN surface without the formation of new defects. In this letter, we propose a method to perform such low temperature oxidation by exposure to ozone and describe the influence on the electrical transport properties of InN.

The InN layers were grown[16] in a Balzers MBE system using conventional effusion cells for In and Al and a rf nitrogen plasma source. All InN epilayers were grown on 200–300 nm AlN at ~380 °C under stoichiometric (1:1) conditions. The InN layers had a thickness of th ~300–1100 nm and a surface roughness rms of ~1–13 nm. In addition, InN was grown by migration enhanced molecular-beam epitaxy on *in situ* prepared 220 nm Ga-face GaN buffer layers[2] with $th = 1800$ nm and rms of ~0.8 nm. The basic film properties were reported elsewhere.[16–18] The electron properties were determined before and after the oxidation experiments by Hall measurements at 0.4 T in van der Pauw geometry with In point contacts.

For oxidation, the samples were exposed for 30 s to UV light ($\lambda \sim 375$ nm) using a commercial light emitting diode. Then, a gas mixture of N_2, O_2, and O_3 was flown over the sample for 60 s. This cycle was repeated for several hours until the resistivity of the sample saturated. The oxidation process was monitored *in situ* by measuring the resistance between In contacts (Fig. 1). Obviously, the resistivity drops during the first few UV/ozone oxidation cycles. By Auger electron spectroscopy (AES) a decreased carbon concentration (resulting from the always present contamination from the environment) and slight oxygen enrichment were found. A cleaning effect by ozone as the reason for the observed decrease of resistance is unlikely, since desorption of water or polar carbon containing molecules (hydrocarbon, CO_2) should result in an opposite effect on the resistance.[19] Oxygen diffuses into the surface without the formation of an indium oxide. Such oxygen was shown to act as donor[7,8] and, consequently, enhances the free electron concentration close

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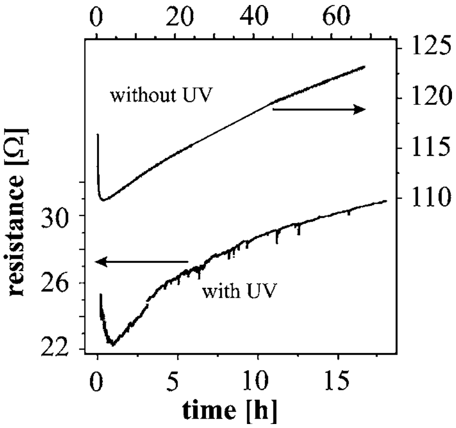

FIG. 1. Resistivity of InN layers vs time during oxidation in ozone (upper curve) and the UV/ozone cycling oxidation (lower curve) of a 1000 nm thick InN film demonstrating that the UV assisted oxidation is faster. Top and right scales correspond to the upper curve. The change in the absolute resistance is caused by the different contact geometry.

to the surface. Further oxidation reverses the trend and the resistance continuously increases with the transformation of the InN surface into a thin oxide film. When exposing to ozone without intermediate UV illumination (Fig. 1, upper curve), the InN surface oxidizes in a similar way; however, it requires a longer time until saturation of the resistance is observed.

The transport properties of the InN films, as grown and after the UV/ozone oxidation, were measured in dependence on the temperature from 100 to 300 K. They revealed that the observed higher resistance of the InN film after the ozone oxidation is attributed to an improvement of the transport properties. At room temperature, for a 1000 nm thick InN the electron mobility raised upon oxidation from 1140 to 1230 $\text{cm}^2/\text{V s}$, while the electron concentration drops from 1.3×10^{18} to 1.1×10^{18} cm^{-3}. The most striking result of these measurements is the reduction of the corresponding sheet carrier concentration of about $(2 \pm 0.5) \times 10^{13}$ cm^{-2} independent of the temperature (Fig. 2, insert). This value is very close to the measured sheet charge density for the free electrons accumulated at the surface[7,10] ($N_{S,0} = 2.4 \times 10^{13}$ cm^{-2}) and was determined for all InN samples with a thickness of >700 nm (Fig. 2). Since the oxygen can penetrate only the InN surface, a very effective passivation of the surface occurs. AES measurements revealed the existence of a closed oxide layer on top of the InN; however, this indium oxide is not a cubic In_2O_3.

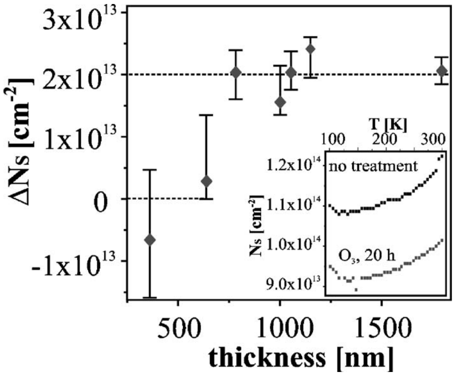

FIG. 2. Difference of the sheet electron concentration ΔN_S for InN films before and after ozone oxidation vs film thickness. Inset: sheet carrier concentration N_S vs temperature for a 1000 nm InN film before and after oxidation, which shows that ΔN_S is independent of the temperature.

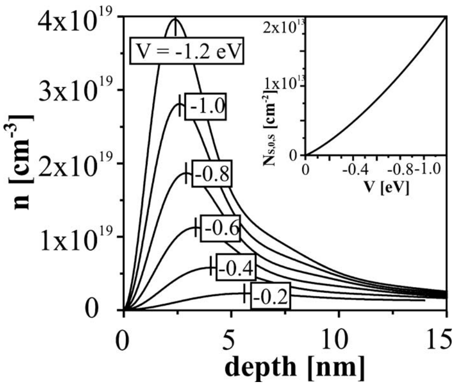

FIG. 3. Electron density distribution n vs depth beneath the surface calculated for different values of the surface band bending V (in eV) for a background doping of $n \sim 10^{18}$ cm^{-3}. Inset: Sheet density $N_{S,0,S}$ of the accumulated carriers due to the surface band bending V. $N_{S,0,S}$ is the sheet carrier density obtained by integration of the profile subtracted by the value due to the background doping n (th=200 nm).

For the explanation of the effect of the ozone stimulated oxidation, two mechanisms are possible. First, a saturation of the In bonds on the surface by oxygen leads to a reduction of the density of surface states and consequently, in a reduced band bending. On the other hand, the thin oxide could exhibit bulklike properties. The conduction band offset is as high as about 2 eV, and the native doping of the wide band gap indium oxide (3.7 eV for In_2O_3) is n type. Thus, for an InO_x/InN heterojunction an even stronger electron accumulation could be expected. Therefore it can be concluded that the ozone stimulated oxidation indeed passivates the surface, however, the exact mechanism requires further investigation by electron spectroscopy.

The observed improvement of the transport properties is caused by two effects. First, if a two layer model for the electronic properties is taken into account, the film mobility μ is given by $\mu = \Sigma_i \mu_i^2 n_i / \Sigma_i \mu_i n_i$, where μ_i and n_i are the electron mobility and concentration of the ith layer, respectively. However, reasonable values for the mobility of the accumulation layers, $\mu \sim 300$ $\text{cm}^2/\text{V s}$, taken from the multiple field Hall measurements of Swartz *et al.*,[20] and sheet carrier concentrations for the surface and the interface[5] of $N_{S,0,S} = 2.4 \times 10^{13}$ cm^{-2} and $N_{S,0,I} = 2.4 \times 10^{13}$ cm^{-2}, respectively, underestimate the mobility improvement for thicker InN layers. Thus, a second effect has to be considered.

The high degree of passivation at the surface results in a decreased surface band bending, which was measured to be about −0.9 eV at the clean[7] and the air-exposed InN surface.[10] By numerically self-consistent solution of the Schrödinger and Poisson equations (Fig. 3), for the remaining electron accumulation of about 5×10^{12} cm^{-3}, a band bending of less than −0.4 eV was determined after the ozone treatment. Figure 3 also demonstrates that with lower band bending the maximum of the electron concentration is shifted into the bulk from ~2.5 nm of the as grown InN to ~5.5 nm for the oxidized InN. These electrons are less affected by the surface roughness, i.e., the mobility should increase. For the investigated InN samples with a rms of ~1–13 nm, this effect should be more pronounced for the smoother InN (rms of ~1–3 nm) films, which was qualitatively confirmed by the experiments. For quantitative analysis of the effects, Monte Carlo simulations will be necessary. Finally it should be noted that for thin InN films with lower structural quality, the improvement of the transport properties is less pronounced or even negligible (Fig. 2), which might be caused by the high dislocation density.

In conclusion, a room temperature ozone stimulated oxidation of thin InN films is proposed, which improves the transport properties and decreases the surface accumulation of free electrons in high-quality InN. The increased electron mobility is caused by the reduced number of “slow” electrons at the InN surface and the shift of the maximum electron concentration from the surface into the bulk upon the reduced surface band bending, which decreases the surface scattering. The reduction of the sheet carrier concentration after oxidation is close to the value of the intrinsic surface accumulation of free electrons in InN, which implies that the ozone treatment effectively passivates the surface. This opens the way to electronic applications where the high n doping of the surface was a strong drawback. In particular, it should enable to contact directly p-type InN, which up to today could be identified only indirectly. However, for an application the stability of the surface oxide has to be investigated. First observations indicate a slight degrading of the transport properties in time (about 25% for a smooth sample after several months). The stabilization with additional top layers will be the task of the ongoing studies.

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