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Probing and modulating surface electron accumulation in InN by the electrolyte gated Hall effect

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The surface contribution to the electrical transport properties of InN was directly measured and modulated by the electrolyte gated Hall effect. Undoped and Mg-doped films show different behaviors that can be effectively described by a multilayer model, taking into account the conduction contribution from both the surface and interface with the buffer layer. Gated photoluminescence experiments further show the surface accumulation layer enhances radiative electron-hole recombination in undoped InN. © *2008 American Institute of Physics*.

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$In_{1-x}Ga_xN$ alloys feature a bandgap ranging from the near infrared to ultraviolet, making them useful for wide-spectrum light emitting diodes and solar cells.[1] However, commercial devices have only been made using Ga-rich alloys, and unsolved materials issues, such as *p*-type doping and surface Fermi level pinning, currently prevent fabrication of devices with In-rich alloys.

Undoped InN films always show *n*-type conductivity. This effect has been attributed to the unusually low conduction band minimum (CBM) in InN, more than 0.9 eV below the Fermi-stabilization energy (E_{FS}).[2] This causes native defects in InN to act as donors, resulting in a high background concentration of electrons. Surface states in InN pin the surface Fermi level slightly below E_{FS}, leading to an ~5 nm thick surface electron accumulation layer (the thickness varies depending on bulk carrier concentration) with a sheet carrier density of the order of 10^{13} cm^{-2}.[3] The surface accumulation layer is always present except for nonpolar planes cleaved under high vacuum.[4] No chemical passivation has been found to remove this layer, although some surface treatments can affect its properties.[5,6] Additionally, electron accumulation has been observed on the back interface between the InN film and the buffer layer (typically GaN or AlN).[7]

The surface and interface accumulation layers contribute significantly to the measured electrical properties of InN, particularly for thin films (<200 nm). Additionally, the accumulation layers result in *n*-type Hall voltages for Mg-doped InN, even though other experimental techniques have found bulk *p*-type conductivity.[8,9] In this letter, we show that the electron density in the surface layer can be modulated using a gate voltage applied to a KCl electrolyte, providing a direct way to probe the electrical properties of the surface and interface accumulation layers.

InN films were grown by molecular-beam epitaxy on *c*-plane sapphire substrates.[10] Two different InN samples are discussed in this paper: an unintentionally doped 120 nm film grown with a 180 nm AlN buffer and a 500 nm Mg-doped film grown with a 240 nm GaN buffer. The Mg content was measured by secondary ion mass spectrometry to be $\sim 10^{21}$ cm^{-3}. Electrochemical capacitance voltage measurements indicated bulk *p*-type doping in the Mg-doped film used in this study.[9]

Gated Hall effect measurements were performed on both samples using $0.01M-1M$ KCl electrolyte solutions using a platinum counterelectrode. Figure 1(a) shows the experimental setup. The sample potential was measured with respect to a saturated calomel electrode (SCE). Electrolyte gated Hall effect has been used to determine transport properties under gating conditions in other materials, such as ZnO,[11] but not in InN. The samples were prepared in the van der Pauw geometry using indium contacts covered with picene wax. The wax is necessary to prevent the current from flowing between the contacts and counterelectrode. Gate voltages were varied only in a current blocking regime (typically ±1 V versus SCE) to avoid any electrochemical reactions that could affect surface measurements. Hall effect measurements were performed with an Ecopia HMS-3000 system. Hall currents between 0.2 and 1 mA were used. Measurements were only taken when leakage currents were at least one order of magnitude lower than the Hall currents. Carrier concentra-

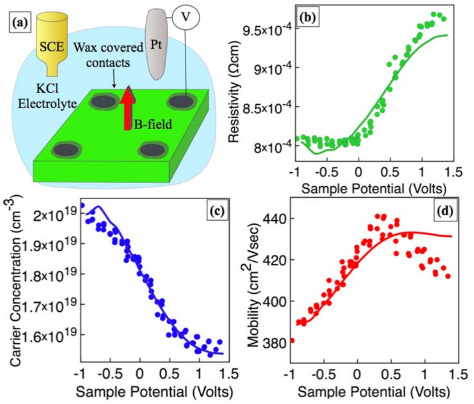

FIG. 1. (Color online) (a) Electrolyte gated Hall effect experimental setup. (b) Resistivity, (c) carrier concentration, and (d) mobility of an undoped InN film as function of potential measured with respect to the SCE. Solid lines are multilayer model fits.

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tions were calculated by dividing the measured sheet carrier concentration by the sample thickness. The measured carrier concentration includes contributions from the surface, bottom interface, and bulk of the film.

Figure 1 shows the change in resistivity, carrier concentration, and mobility of the undoped InN sample with gate biasing. Figure 1(b) shows that the resistivity is changed by ~21% under positive sample biasing. Figure 1(c) shows the reduction in electron concentration of the sample under positive biasing. The sheet charge density decreased by 3×10^{13} cm^{-2} when the voltage was varied from 0 to 1.4 V, consistent with the expected sheet density of surface electrons.[3] The carrier concentration modulation, rather than the mobility modulation, is predominantly responsible for the change in resistivity. Two other undoped InN samples (not shown here) exhibited similar behavior.

The data were fit using a multilayer model describing the contributions to the overall measured concentration and mobility from the surface, bulk, and interface.[12] To calculate the contribution from the surface layer, the surface Fermi level was assumed to be 1 eV above the CBM. The electron distribution was calculated using the semiconductor finite element analysis software CROSSLIGHT using a nonparabolic band with an effective mass of $0.05m_0$ at the CBM.[13] The carrier concentration of the surface layer was then taken as the average carrier concentration over the first 5 nm.

A bulk (interface) carrier concentration of $10^{19}(1.5\times10^{20})$ cm^{-3} and mobility of 450 (400) cm^2 V^{-1} s^{-1} were estimated by fitting the carrier concentration and mobility data. For the purpose of modeling the experimental results, the back interface accumulation region was assumed to be similar in nature to the surface accumulation region and was 5 nm thick. Some authors proposed the interface accumulation region results from a high density of dislocations at the interface[7,14] or from unintentionally incorporated impurities,[15] which would extend some distance into the film. Additionally, it has been observed that different growth conditions for InN can alter the number of interface electrons.[16] Experimentally, we are unable to separate the bulk carrier concentration from the interface accumulation and therefore cannot determine the origin or spatial extent of the interface accumulation layer.

The model was found to best fit the data with a surface mobility linearly decreasing with negative sample biasing. This decrease in surface mobility under negative sample biasing is likely caused by the electrons accumulated closer to the surface where they are more effectively scattered by surface states. The multilayer model semiquantitatively fits the change in measured carrier concentration and mobility (lines in Figs. 1 and 2). It should be noted that the present model is only qualitative, and a more rigorous approach to modeling the transport properties would require taking into account the quantum confinement of the surface electrons[17] as well as the spatial extent of the additional interface electrons.

Figure 2 shows the effect of gate biasing on the Mg-doped InN. Despite the entire sample being immersed in electrolyte, the film still remains *n*-type under large positive biasing. This indicates that the back interface (with electron accumulation unaffected by gating) is still electrically connected to the contacts on the surface, possibly because the sides of the film are not fully depleted or due to conductive vertical dislocations that run through the film. The data were again fit using the multilayer model with two contributing thin layers: surface and interface, as shown by the solid lines. Figure 2(a) qualitatively shows the variation in electron and hole densities for a Mg-doped InN sample with a bulk hole concentration of 5×10^{19} cm^{-3}. The bulk *p*-type material is assumed to be electrically isolated from the *n*-type surface and interface by a depletion region. Upon sufficient positive biasing, the surface layer is completely depleted leaving only the interface layer contributing to the sample conductivity. The flat carrier concentration and mobility under positive bias in Fig. 2 can be attributed solely to the interface conduction. The sheet carrier concentration and mobility of the back interface are thus found to be 1.2×10^{14} cm^{-2} and 60 cm^2 V^{-1} s^{-1}, respectively. However, if bulk holes were contributing to the electrical conduction, the positive Hall voltage could partially offset the Hall voltage of the interface layer, leading to an underestimation of the interface mobility and an overestimation of the interface accumulation. Another *p*-type sample (not shown) exhibited a similar flat region of mobility and carrier concentration, although at a 0.4 V higher gate voltage. The increase in mobility upon negative biasing [Fig. 2(d)] shows that the interface mobility is lower than the surface mobility possibly due to a different origin of electrons at the surface and interface.

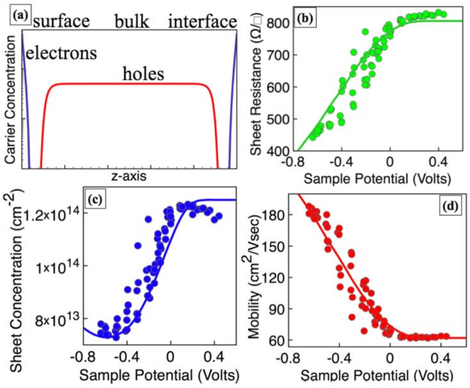

FIG. 2. (Color online) (a) A schematic qualitatively showing the variation in electron and hole density throughout the Mg-doped InN sample. (b) Sheet resistance, (c) sheet concentration, and (d) mobility of a Mg-doped sample as a function of potential measured with respect to SCE. Solid lines are multilayer model fits.

Electrolyte gating was also used to measure the effect of surface accumulation on photoluminescence (PL). A quartz crucible was used to immerse the undoped sample in a 0.01*M* KCl solution. A 488 nm argon laser provided the excitation source; PL was detected with a Ge detector cooled with liquid nitrogen. Figure 3 shows the change in PL spectra with a +1 V bias between the sample and counterelectrode.

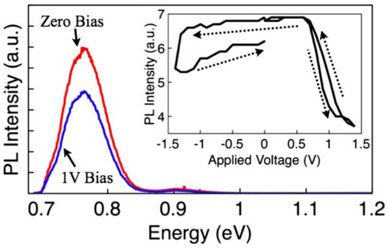

FIG. 3. (Color online) PL spectra for the undoped sample under 0 and +1 V bias. The inset shows PL peak intensity vs applied bias. Biasing beyond −0.5 V yielded an irreversible PL intensity drop accompanied with a large leakage current (not shown).

The peak position PL intensity was measured while varying the gate bias (Fig. 3, inset). A 45% drop in PL was seen under a 1.4 V applied bias. This PL intensity drop was reversible upon removing the bias voltage. However, under strong negative bias, an irreversible PL drop was measured along with a large leakage current. This is likely due to photoetching of the sample. The PL intensity drop under positive biasing, i.e., under surface band flattening conditions, is consistent with the model in which strong PL in unbiased *n*-type InN results from a surface field induced drift of photoexcited holes into the bulk away from the surface recombination centers. Under positive bias conditions, the holes remain closer to the surface and have a larger probability of nonradiative recombination through the surface states.

In summary, electrolyte gated Hall effect has been used to modulate the electrical conduction through the surface layer of InN. This technique was used to evaluate the magnitude of surface electron accumulation and also to measure the interface electron accumulation existing in Mg-doped InN films. Gated PL measurements show that the removal of the electron accumulation layer causes reduction in PL intensity.

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