InN-based anion selective sensors in aqueous solutions

Yen-Sheng Lu, Chi-Cheng Huang, and J. Andrew Yeh
Institute of Electronics Engineering, National Tsing-Hua University, Hsinchu, 30013 Taiwan

Chi-Fan Chen and Shangir Gwo
Institute of Nanoengineering and Microsystems, National Tsing-Hua University, Taiwan and Department of Physics, National Tsing-Hua University, Hsinchu, 30013 Taiwan

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We demonstrate that indium nitride (InN) can be used as ion selective electrode (ISE) for anion concentration measurements. The InN ISE reveals remarkable selectivity, response time, signal stability, and repeatability for chloride and hydroxyl ions. The selective interaction of Lewis bases in solutions with the N-polarity InN epitaxial layer grown on silicon is confirmed by potentiometric responses. The Helmholtz potential of the InN ISE, generated at the InN/solution interface, satisfies the Nernst equation. The observation of anion attraction to the InN surface further demonstrates the existence of donor-type surface states on InN. © 2007 American Institute of Physics. [DOI: 10.1063/1.2814035]

Recent advances in the epitaxial growth techniques of indium nitride (InN) have made it possible to study the unusual optical and electronic properties of InN. For example, it has been shown that as grown, nominally undoped InN films exhibit a large free electron concentration (typically in excess of $1 \times 10^{18}$ cm$^{-3}$). In addition, intrinsic electron accumulation at InN surfaces has been confirmed by various experimental techniques. These electronic properties are believed to be related to the unusually low conduction band minimum of InN at $\Gamma$ point, resulting in the highest electron affinity among known semiconductors and the Fermi-level stabilization energy ($E_{\text{FS}}$) deep inside the conduction band. It has been argued that, when the location of Fermi energy is below $E_{\text{FS}}$, the native defects in InN tend to become positively charged donor states, giving rise to the phenomena of high $n$-type background concentration and surface electron accumulation. Recently, the ab initio calculations of InN electronic structure have also confirmed that positively charged surface donor states exist on InN for emitting electrons into the conduction band. Moreover, King et al. have reported the universal electron accumulation phenomenon at the grown surfaces of wurtzite {1120} (nonpolar, $a$ plane), (0001) (In polar, $+c$ plane), and (000$\bar{1}$) ($N$ polar, $-c$ plane) InN prepared by atomic hydrogen cleaning. This surface electron accumulation phenomenon can cause a downward band bending of about $0.7$ eV in the near-surface region of InN. Jones et al. have also shown that surface electron accumulation at the InN surface is not affected by doping. While the exact microscopic nature of these surface states may vary between differently prepared surfaces, the bulk band structure of InN seems to dictate that electron accumulation will be present at all surfaces provided the bulk Fermi level lies below the charge neutrality level.

This electron accumulation phenomenon is very unusual among III-V semiconductors. For example, the degree of band bending on GaN surfaces (upward band bending for $n$-type or as-grown $c$-plane GaN) depend on crystal polarity, charged dopants (downward band bending for $p$-type $c$-plane GaN), defects, adsorbates, surface states, and surface treatments (cleaning, etching, annealing, passivation, ultraviolet light illumination, etc.). For InN, the efforts to eliminate the surface electron accumulation effect by chemical or physical treatments have not been successful. The positively charged donor surface state density was found to be as high as the order of $10^{13}$ cm$^{-2}$ (the largest native electron accumulation observed at III-V semiconductors). Although the surface electron accumulation effect is detrimental to the realization of InN-based devices requiring both $n$- and $p$-type doping, the high surface charge density and robust surface properties of InN are beneficial for sensor applications. Indeed, InN material has been proposed to be useful for sensing applications. In principle, the positively charged surface donor states of InN should allow negatively charged ions in solutions to be selectively attracted to the InN surface.

Ion selective electrode (ISE) based potentiometric sensors have been developed for chemical, biomedical, physiological, and clinical applications. Ligands, functionalized groups or ionophores absorbed on the ISE selectively respond to surrounding specific ions, resulting in the change of the ISE’s surface potential. Both sensitivity and selectivity of such a response is primarily determined by the composition and polarity of the ISE. To achieve high sensitivity, good repeatability, and fast response, the use of solid-state materials with high electron mobility, such as III nitrides, have also been proposed. For example, the anion-selective adsorption to GaN has been reported to induce a potential within the Helmholtz layer (1 nm) and the diffuse Gouy layer (10 nm) and brings out realization of GaN ISEs. In this study, InN ISE is demonstrated by us for selectively determining anion concentrations, such as chloride (Cl$^-$) and hydroxyl (OH$^-$) ions, in aqueous solutions by using potentiometric measurements.

The heteroepitaxial growth of InN on the Si(111) substrate was conducted in a molecular-beam epitaxy system equipped with a radiofrequency nitrogen plasma source. InN epilayers were grown by a two-stage growth method using an AlN buffer layer on the surface of $\beta$-Si$_3$N$_4$(0 0 0 1)/
IIA chlorides, respectively. Hydroxyl ions showed a similar potential buildup and the volume concentration, respectively. The sensitivities, the slopes of the fitted lines, were determined to be $-47$ and $-45$ mV/decade at 25 °C for the IA and IIA chlorides and hydroxides, respectively.

The sensitivities of $-49$ mV/decade for the IA and IIA chloride solutions and hydroxyl solutions, respectively. The potentiometric responses of InN ISE to various concentration measurement of either hydroxyl ion concentrations, $E = -47 \log C - 490$ (mV), $E = -45 \log C - 503$ (mV), and $E = -49 \log C - 508$ (mV) with weight sum of squared residuals set at $2 \times 10^{-5}$. The parameters $E$ and $C$ indicate the potential buildup and the volume concentration, respectively. The measured potentials of the InN ISE are linearly proportional to the logarithm of volume concentration, satisfying the Nernst equation. The lines that were fitted using the nonlinear least squared method can be expressed as $E = -47 \log C - 490$ (mV), $E = -45 \log C - 503$ (mV) and $E = -49 \log C - 508$ (mV) with weight sum of squared residuals set at $2 \times 10^{-5}$. The parameters $E$ and $C$ indicate the potential buildup and the volume concentration, respectively. The sensitivities, the slopes of the fitted lines, were determined to be $-47$ and $-45$ mV/decade at 25 °C for the IA and IIA chlorides and hydroxides, respectively. Hydroxyl ions showed a similar sensitivity of $-49$ mV/decade. The repeatability measurement of the InN ISE yielded the potential variation of $\pm 1$ mV. The long-term stability was found to be 9 mV for 6 h, which is close to the GaN ionic sensors. Negative sensitivity implies that the potential shifted to more negative as the chlorine ion concentration increased. This result suggests that the InN ISE selectively respond to chlorine ions instead of cations, resulting from the chlorine ions attracted to the positively charged donor sites on the InN surface. Note that the theoretical sensitivity of single charged cations (e.g., K+, Na+, and NH4+) is twice as much as that of double charged cations (e.g., Ca2+ and Ba2+), according to the Nernst equation.

Dynamic response of the InN ISE for potassium chloride (KCl) of 0.01 M → 0.05 M → 0.1 M and 0.01 M → 0.1 M is plotted in Fig. 2. The fall (capture) time and the rise (recovery) time indicate the times elapsed after the ion concentrations change from 10% to 90% and from 90 to 10%, respectively. Both the fall time and the rise time of the one-decade volume concentration change (e.g., 0.01 M → 0.1 M) are found to be 12 and 78 s for the IA chloride solutions and to be 18 and 108 s for IIA chloride solutions. The fall time is faster than the rise time for the tested chloride solutions by roughly six times. Overall, both the short response times and the long-term potential stability suggest that the potential buildup mechanism results from purely a surface mechanism without bulk transition into InN crystals.

Both charged donors from extrinsic donor impurities and donor-type native surface/bulk defects at and near the surface region may provide charged sites that selectively adsorb anions on the InN surface, building a Helmholtz voltage in the electrolyte. The adsorption of anions to positive charged donors expels the accumulated electrons in the near surface region. To further verify the uniqueness of anion coordination, the InN ISE was tested in pH buffer solutions with pH values of 2–10 (HANNA Instruments). Figure 3 shows that the InN ISE does not react to hydrogen ions (H+). In contrast to GaN ISE, InN ISE exclusively binds with anions due to its unusual surface accumulation properties. GaN ISE has been demonstrated for concentration measurement of either hydrogen ions or anions because both upward and downward band bendings can exist at GaN surfaces.

In summary, the N-face InN film grown on silicon substrate has been demonstrated to be an excellent sensing element that can selectively react to anions in aqueous solution.
tions. The InN ISEs are selective to anions instead of cations because the IIA and IA salts have the proportional sensitivity in anion stoichiometry. The \( N \)-face InN ISE showed good characteristics of fast response, long-term stability, and high repeatability. The sensitivity measured is caused by direct interaction between anions and positively charged surface donor states on InN, which function as fixed surface sites for the reversible anion coordination. The experimental result of selective anion attraction to the native InN surface further confirms the existence of positively charged donor states on the InN surface.

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