Journal of New Materials for Electrochemical Systems 13, 337-343 (2010)

Electrochemical Characterization of InN Thin Films for Biosensing Applications

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Received: November 20, 2009, Accepted: October 27, 2010, Available online: December 07, 2010

Abstract: *InN, a well-established optoelectronic material, is currently being considered as a promising material for sensor applications. In this study, the fundamental electrochemical properties of InN thin film and its potential for electrode chemical and bio-sensing applications are demonstrated. The cyclic voltammograms of different concentrations of dopamine solution in 1 M $HClO_4$ were measured. Similarly, potentiostatic measurements at 1 V versus Ag/AgCl show stable responses and linear change of current density with concentrations up to 0.475 mM dopamine. The InN thin film also demonstrated repeatable positive photoresponse to cathodic currents in 1 mM $Ru(NH_3)_6^{3+}$ in 1M KCl solution under a 100 mW cm^{-2} 808-nm laser light illumination at a constant -0.25 V (vs. Ag/AgCl) bias. The cathodic current response showed a 27% enhancement, demonstrating its potential as photocathode. This cathodic photocurrent behavior is explained through the electron accumulation of the InN material.*

Keywords: biosensor, potentiostatic measurements, dopamine detection, biocompatibility, photoresponse

1. INTRODUCTION

Aside from their potential applications in solar cells and other optoelectronic devices, the III-Nitride materials have also drawn tremendous attention towards the chemical and biological sensing applications. Much of the anticipation on III-Nitride being a good sensing material lies on their chemical stability and biological compatibility[1]. AlN[2] and GaN[3, 4] have been demonstrated to be pH sensitive and suitable for biosensing[5, 6]. Recently, GaN and InN were reported to be suitable matrices for urease immobilization while remaining sensitive to the pH of the environment.[7] Ga-terminated GaN films have also been reported as sensitive to various anions in solution[8]. Recently, wurtzite AlGaN/GaN heterostructure field effect transistors has been demonstrated to be ion-sensitive and the surface can be modified to introduce selectivity to pH levels[3] and proteins[9]. However, most of the studies on the sensing applications of III-Nitrides have been focused on GaN probably because of the maturity in its device fabrication processes; whereas AlN and InN have lagged behind. Nevertheless, as understanding in their production becomes more and more developed, the number of studies exploring the sensing capabilities of InN and AlN is expected to increase.

As part of the III-Nitride group, InN, in particular, has also been considered as a promising material for sensor applications[10]. Studies initially conducted by Lu, et al reported that InN shows fast-capture, slow release, responsivity and selectivity to certain solvent chemical exposures[11]. Recently, Pt-coated InN nanorods were discovered to be H_2 gas sensitive [12, 13]. Nanostructured InN and its junctions with other nitride materials, which open the possibility of utilizing high surface area for sensing applications, have also been reported.[14-17] The main advantage of InN over the other III-Nitrides is the presence of a strong and intrinsic electron accumulation at the wurtzite InN surface.[18, 19] Presence of charge-accumulation at the surface, especially in a polar system like InN, results the generation of surface-depletion region, in which charges are spatially separated. Consequently, this can po-

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tentially provide higher sensitivities at InN surface because adsorption/absorption of foreign ions at the surface can affect the depletion width, thereby modulating the surface-dominated properties of InN. An additional advantage to InN is the natural formation of thin oxide layer at its surface under ambient conditions, which can assist in selective surface-functionalization. Functionalizations of InN surface[20] opens up the possibility of various potential applications, including the immobilization of chemical/biological molecules, which can be utilized for high-sensitivity chemical and biosensing applications. Most importantly, InN possesses chemical stability and biocompatibility like other III-nitrides.

In this paper, we present the electrochemical properties of InN thin film that strongly suggests a possible transduction strategy for the InN surface. The sensing mechanism for InN so far has been restricted to the detection of the changes in bulk-conductivity as it is exposed to various target analytes. Studies on the utilization of electrochemical methods as transduction methods for InN sensing applications have been limited.

Electrochemical studies provide the additional information on the conduction of InN in solution as the electron-transfer at semiconductor-solution interface is accounted for in electrochemical measurements. The variations in applied potential can induce various interfacial chemical reactions, easily detectable in electrochemical methods but may not be obvious in the measurement of conductivity within the bulk-material itself. Electrochemical methods, furthermore, presents the additional advantages of high sensitivity, economy, ease of miniaturization, and direct electronic readout. The use of semiconductors as an electrode can provide the additional advantage of wide electrochemical windows compared to metals as the potential for water dissociation can be suppressed. Furthermore, being an optoelectronic material, InN electrode should provide an advantage of utilizing photo-assisted electrochemical technique, which would definitely lead to the enhanced sensitivity in electrochemical response/sensing.

2. EXPERIMENTAL

2.1. Synthesis of InN thin film by Gas-Source Molecular Beam Epitaxy

In this study, InN epitaxial films were deposited on sapphire templates using gas-source molecular beam epitaxy (GS-MBE) system. The base pressure of the growth chamber was pumped to 3×10^{-10} Torr. Indium source was evaporated and ejected from a conventional Kundsen cell (K-cell), while nitrogen source was supplied from highly volatile HN_3 precursor during the growth process. The substrate temperature is 450°C, the K-cell temperature is 850°C, and the nitrogen/HN_3 pressure is 2.5×10^{-6} Torr. The detailed process is given elsewhere [21].

2.2. Preparation of InN electrode

InN electrode was prepared by bonding a copper wire onto the edge of InN thin film (approximately 0.5×0.5 cm^2). The bonding was done by applying silver paste, and finally cured at 80°C for 20 minutes. The bonding pad, side-edges and backside were covered with epoxide in order to expose only the InN-surface with desired area (approximately 0.4×0.4 cm^2 for the cyclic voltammetry tests and 0.2×0.2 cm^2 for the light response) to the test solutions. This ease of making an electrode with Ohmic contact is one of the advantages of InN over the other III-Nitrides. Unlike AlN and GaN, binding metallic wire using common silver glue would be enough to establish an Ohmic contact on InN.

2.3. Determination of Electrochemical Properties

All electrochemical experiments were done using Electrochemical Multichannel Machine Solartron Analytical 1470 E Cell Test System, using the three-electrode system, with Ag/AgCl reference electrode and Pt sheet as the counter electrode. All the chemicals used were reagent grade: H_2SO_4 (95-97%, Acros), $HClO_4$(70%, redistilled, Aldrich), KOH (>99%, Acros), $K_4Fe(CN)_6{\cdot}3H_2O$ (>99.0%, Showa), $Ru(NH_3)_6Cl_3$ (98%, Aldrich), 3-hydroxytyramine hydrobromide (99%, Aldrich), NaH_2PO_4 (>98%, Sigma), KCl (>99.5%, Ferak) and $Fe_2(SO_4)_3{\cdot}5H_2O$ (97%, Aldrich). Distilled deionized water (resistivity = 18.2MΩ cm) was used for preparation of solutions and for rinsing InN electrode prior to each run. All the measurements were done in covered containers in order to avoid the effects of the ambient light on InN measurements.

2.4. Determination of Potential Window and of ΔE_p

In order to gauge the extent to which InN films would be suitable for electrode applications, the working electrochemical potential window in phosphate buffer solution (PBS) at pH 7 was determined. To test the reversibility of the electron transfer in the InN electrode, the cyclic voltammetry profile in 5 mM $Fe(CN)_6^{4-/3-}$ (in 1M KCl) under varying scan rates were measured.

2.5. Electrochemical Response to Different Chemicals

To demonstrate the electrochemical activity of InN electrode, two other well-known aqueous-based redox systems, $Ru(NH_3)_6^{3+/2+}$, and $Fe^{3+/2+}$, were used. To demonstrate its aptness for biosensor applications, the cyclic voltammetric sensing to common biochemical dopamine was measured.

In order to gauge its biosensing properties, the cyclic voltammetry profiles of the electrode at different concentrations (0.01, 0.1, 1 mM) of dopamine in 1 M $HClO_4$ were measured. Moreover, in order to demonstrate the stability and linearity of the electrochemical response, potentiostatic measurements at 1 V versus Ag/AgCl reference electrode were tested, under different concentrations of dopamine.

2.6. Photoresponse of InN thin film Electrode

To demonstrate the potential of InN electrode for photo-aided electrochemical reactions, the cathodic current response of InN thin film in 1mM $Ru(NH_3)_6^{3+}$ in 1M KCl solution was measured under the constant voltage of -0.25V (versus Ag/AgCl), in presence of 808-nm laser light with intensity of ~100 mW/cm^2.

To check the band edge potentials of the InN thin film, Mott-Schottky plot was constructed from the capacitance data derived from the electrochemical impedance spectroscopy measurements. The impedance spectra was taken in 1 M KCl solution with an applied potential ranging from 1 to 1.4 V vs. Ag/AgCl reference electrode in 1,000 Hz frequency. Platinum sheet was used as the counter electrode.

3. RESULTS AND DISCUSSION

3.1. Quality of InN thin film

The thickness of c-InN thin film is around 1 μm (measured by

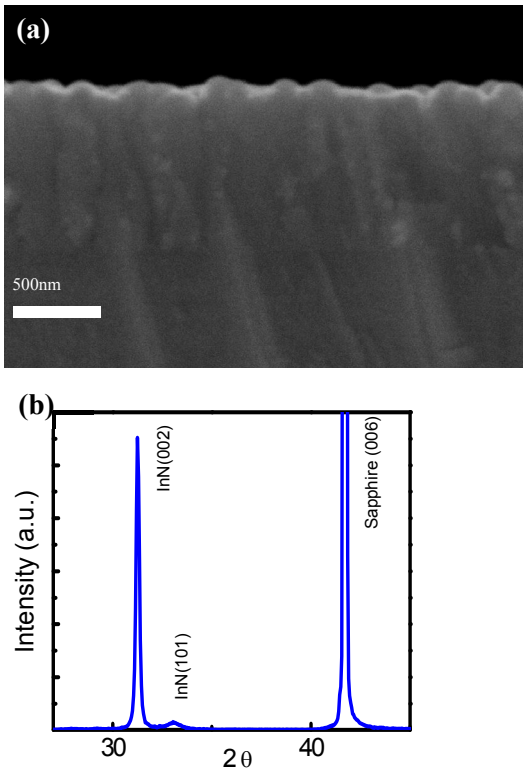

Figure 1. (a) Cross sectional scanning electron microscope image of the InN thin film, (b) X-ray diffraction profile of the InN thin film.

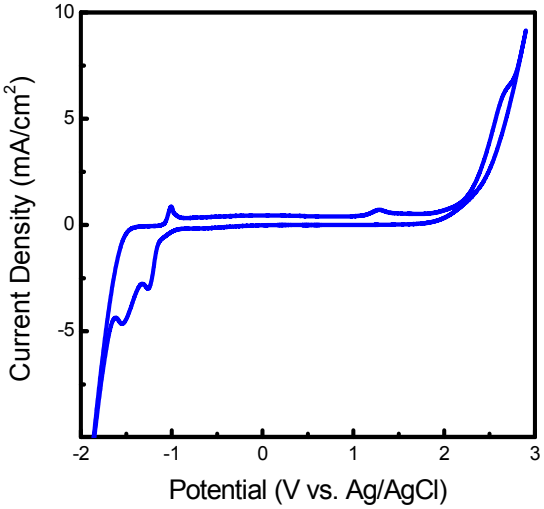

Figure 2. Electrochemical potential window for InN thin film electrode in phosphate buffer solution (pH 7.0). Scan rate, 100 mV/s.

SEM, Fig. 1(a)). The θ/2θ-scan XRD result (Fig. 1(b)) shows a prominent on-axis InN(002) peak at 31.3°and two small peaks at 29.1° and 33.2° corresponding to the off-axis crystal planes of InN(100) and InN(101), revealing the formation of wurtzite InN. The infrared PL measurements showed high quality film with emission peak at 0.705 eV [21].

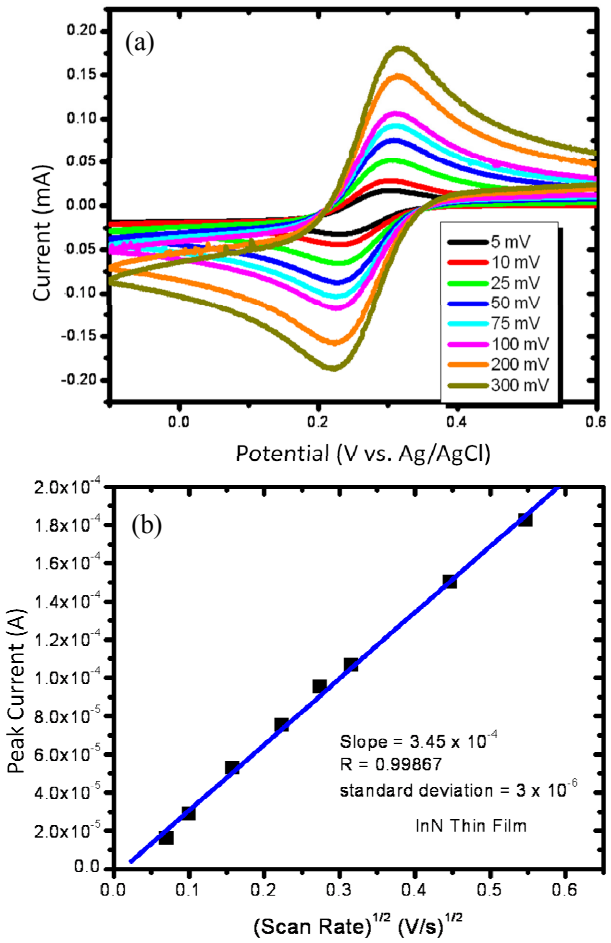

Figure 3. (a) Cyclic voltammetry profile of InN electrode at various scan rates in 5mM $Fe(CN)_6^{3-/4-}$ (in 1M KCl); (b) Oxidation peak current, i_p, versus $(\text{scan rate})^{1/2}$ plot to determine the effective electrode surface area.

3.2. Potential Window

The working potential window is the potential range within which the electrochemical response is highly sensitive to physico-chemical properties of the electrode-surface, without any effect from electrode-material itself due to negligible background current within that range. Outside the window, the background suffers from the presence of several voltammetric features due to multiple electron-transfer steps with direct involvement of electrode-material. The background cyclic voltammetric I-E curves, measured in at 100 mV/s scan rate, revealed a wide workable potential window of about 2.7 V, ranging from -1.5V to 1.2V vs. Ag/AgCl reference electrode (Fig. 2). Literature data shows that this measured potential window under the same conditions is comparable and broader than boron doped diamond (BDD) electrode and MWCNT electrodes. BDD has ~2.55V while MWCNT has ~2.31 V [22].

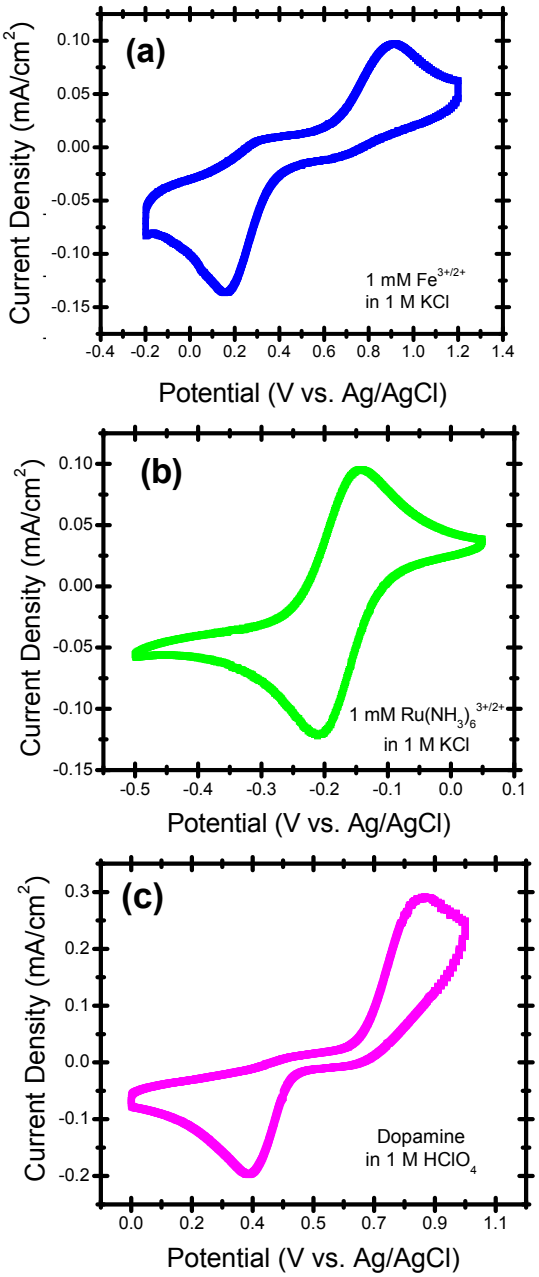

Figure 4. Voltammetric responses, using InN electrode, of various redox-systems, (a) 1mM $Fe^{3+/2+}$ and (b) 1mM $Ru(NH_3)_6^{3+/2+}$, in 1M KCl. (c) Voltammetric Sensing of biochemical 1mM dopamine, in $HClO_4$. Scan rate, 100 mV/s.

3.3. Electron Transfer Reversibility

To test the reversibility of the electron transfer in the InN electrode, the cyclic voltammetry profile in 5 mM $Fe(CN)_6^{4-/3-}$ (in 1M KCl) under varying scan rates were measured (Fig. 3). Reduction (E_R) and oxidation (E_O) peaks at 298 mV and 238 mV, respectively, measured at 5 mV/s sweep rate, indicate nearly Nernstian value for ΔEp ($=E_R-E_O$) (~60 mV) exhibiting fairly fast and reversible electron exchange.

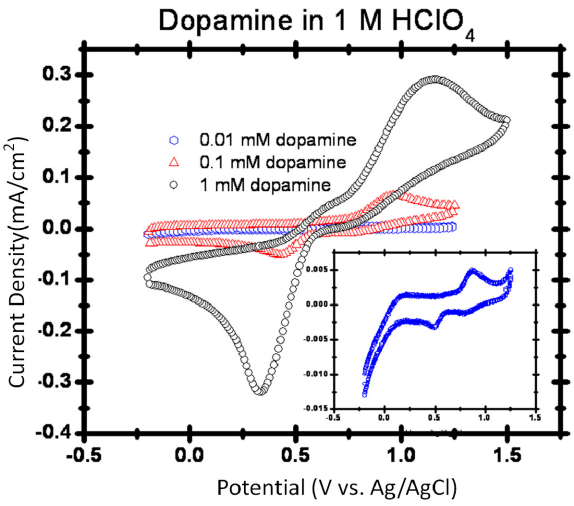

Figure 5. Voltammetric responses, using InN electrode, of biochemical dopamine, in different concentrations at 1 M $HClO_4$. Scan rate, 100 mV/s.

To determine the electrochemical process on the InN film, response to $Fe(CN)_6^{3-/4-}$ was measured under various scan rates (Fig. 3(a)). The square root of the scan rate, $n^{1/2}$, is plotted against i_p, the reduction/oxidation current, as shown in Fig. 3(b). InN shows a good linearity coefficient at 0.9987, indicating the process to be diffusion-limited. This confirms that the electron exchange rate is indeed fast and that the system is controlled by the rate of diffusion of the redox ions in the solution rather than the kinetics of the electron exchange process.

3.4. Responses to Various Redox Chemicals

The use of $Fe(CN)_6^{3-/4-}$ is standard for determining the electron exchange behavior of electrodes. $Ru(NH_3)_6^{3+/2+}$, on the other hand, is another standard electrochemical. These two electrodes were tested to show the versatility of the InN electrode in terms of anionic and cationic oxidation and reduction processes. Earlier reports [23-25] have shown that InN preferentially attracts the anions on its surface, owing to its donor-type surface states. This may be regarded as the reason for good $Fe(CN)_6^{3-/4-}$ behavior. On the other hand, response to $Ru(NH_3)_6^{3+/2+}$ shows that some of the cations can be present at the InN surface as well and have this cations go through reduction and oxidation at the InN surface as well. $Fe^{3+/2+}$, on the other hand, was chosen in order to demonstrate the electrode capacities on a electrochemical that is sluggish in its electron exchange properties. The cyclic voltammograms (Fig. 4(a)-(b) demonstrates the sensitivity/electrochemical response of InN electrode to the reduction and oxidation processes of different redox systems.

The ΔE_p values obtained from these two redox systems are lower than the average values obtained from high quality diamond thin film. ΔE_p of InN thin film in $Fe^{3+/2+}$ solution is 740 mV, broader than the value for multiwall carbon nanotube electrode, while literature value for high quality diamond film 837±42 mV at the same conditions. ΔE_p of InN thin film in $Ru(NH_3)_6^{3+/2+}$ solution is 60 mV, similar to the values measured for multiwall carbon nanotube electrodes, while literature value for high quality diamond film,

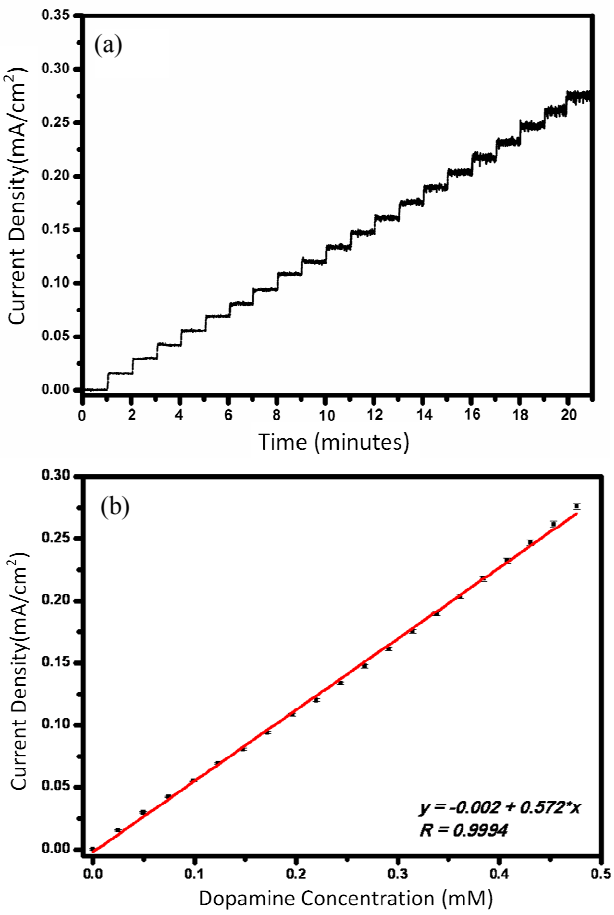

Figure 6. (a) Current density versus time (in mA/cm^2) of the InN electrode, as dopamine is spiked in 1 M $HClO_4$ solution, measured under potentiostatic conditions with 1V applied voltage versus Ag/AgCl reference electrode. Initial volume is 100 mL of 1 M HCl solution, spiked with 0.250 mL of 10 mM dopamine per minute. (b) Average current density versus concentration, as computed from (a), the red line indicates the extrapolated line from the data.

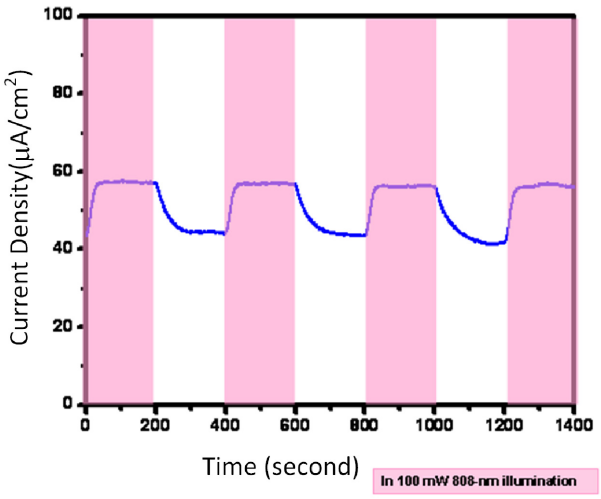

Figure 7. Photo-assisted cathodic current response of InN thin film electrode to 1mM $Ru(NH_3)_6^{3+}$ in 1M KCl solution at constant voltage -0.25V (vs. Ag/AgCl). Shaded area indicates the duration when the electrode is illuminated by 808-nm laser light with intensity of ~100 mW/cm^2.

99±6 mV.[26] The ΔE_p values in the InN thin film indicate slower transfer compared to multiwall carbon nanotubes but faster and more reversible electron exchange compared to diamond film for $Fe^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ electrolytes.

Dopamine was used to demonstrate InN's capacity to detect biochemicals. Dopamine is an important neurotransmitter and is found in patients with Parkinson's disease.[22] The oxidation and reduction peaks for dopamine, in 1 M $HClO_4$, in InN are also well-resolved (Fig. 4(c)). ΔE_p of InN thin film in dopamine solution is 510 mV, a value that is broader than the values for CNT electrodes.[22] However, this value is comparable to literature value for high quality diamond thin film, 509±28, tested at same conditions,[26] indicating InN surface as having comparable reversibility and electron exchange rates to high quality diamond films.

At various concentrations of dopamine in 1 M $HClO_4$, the cyclic voltammograms were measured (Fig. 5). Note that there are corresponding changes in the cyclic voltammograms peaks as the concentration of the biochemical decreases. The inset shows that even at 0.01 mM dopamine, the peaks of dopamine are still well-resolved.

Potentiostatic measurements of the InN electrode with increasing dopamine concentration show increase in current densities at 1 V applied voltage versus Ag/AgCl reference electrode. (Fig. 6(a)) At 1 V applied voltage (versus Ag/AgCl), the InN demonstrates an oxidative current to the dopamine biochemical in solution, as can be seen from the cyclic voltammograms (Fig. 5). Plotting the current density versus the concentration (Fig. 6(b)) shows a linear behavior, up to about 0.475 mM concentrations, with the sensitivity of the system at 0.572 mA cm^{-2} mM, and the linear correlation coefficient at 0.9994.

3.7. Photoresponse

To demonstrate the potential of InN electrode for photo-aided electrochemical reactions, the cathodic current response of InN thin film in 1mM $Ru(NH_3)_6^{3+}$ in 1M KCl solution was measured under the constant voltage of -0.25V (versus Ag/AgCl). (Fig. 7) In presence of 808-nm laser light with intensity of ~100 mW/cm^2, the cathodic current increases from ~45 μA/cm^2 to ~57 μA/cm^2, which corresponds to a 27% increase. The measurements were done at multiple cycles and the positive cathodic current response to light was found to be repeatable.

An earlier study[27] has demonstrated the photoresponse of InN thin film at room temperature in 0.1M KI solution, using white light source with an the same intensity of light. This study, however, having been conducted at a much earlier time, have utilized InN with a higher band gap. The direct band gap of the sample was reported to be 1.8 eV. This study utilized that the low band-gap higher quality films[28, 29] have the potential for use as photoactive cathodic electrodes.

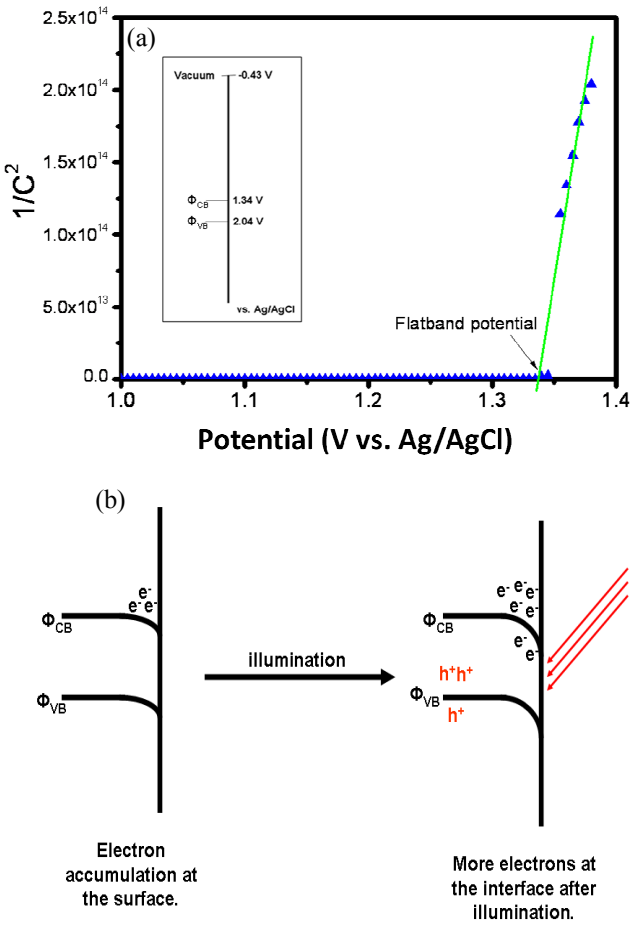

Figure 8. (a) Mott-Schottky plot obtained from the capacitive data derived from electrochemical impedance spectroscopy data at constant 1,000 Hz frequency. Inset: The band edge potentials of commercial InN thin film, where Φ_{CB} is the conduction band, Φ_{VB} is the valence band, versus Ag/AgCl reference electrode in 1 M KCl solution. (b) Schematic of the band bending of InN to explain the photoresponse of InN.

The difference in the photoresponse behavior of the current InN thin film gives further evidence to the degeneracy of semiconducting InN thin film. Mott-Schottky analysis reveal that the flat band potential of the InN thin film is about 1.35 V (versus Ag/AgCl) (Fig. 8(a)), quite consistent to the estimations presented in previous study for InN potential edges [30]. This further confirms that the photoresponse was measured at an inversion region.

Usual n-type semiconductors would demonstrate a photoanodic behavior, similar to earlier studies.[27] The InN thin film demonstrated a positive cathodic probably because of the nature of its band bending and electron accumulation effects. Application of light produces electron-hole pairs that consequently increase the electron concentration at the surface. Increased electron concentration results to greater reductive capacity by the film (Fig. 8(b)).

Moreover, the low bandgap of InN thin film (0.705 eV) and the demonstrated the photocathodic response at low frequency 808-nm light present the additional advantage of wider range of absorption frequencies by the InN film. This presents possible higher efficiency harvests by InN film from visible light compared to higher band gap semiconductors such as ZnO and TiO_2. Moreover, the smaller band gap of InN can provide advantage in photo-activated sensing and study of biomolecules, something that InN electrodes can offer that other common electrodes like multiwall carbon nanotubes and boron doped diamond do not. In addition, the lower energy light used to activate InN means less damage to the biomolecules during photoactivation, as compared to higher frequency light that may easily break molecular bonds.

4. CONCLUSION

The electrochemical measurements on InN thin film electrode have demonstrated its electroactivity to various electrolytes. Consequently, this suggests that InN thin film may be used as an electrode for sensing applications with profile generally similar to that of diamond electrode. Test in biochemical environment, dopamine solution, also demonstrate the suitability of InN for biosensor applications. Moreover, the thin film demonstrated positive photocathodic response to 1mM $Ru(NH_3)_6^{3+}$ in 1M KCl, demonstrating its potential as a photo-active electrode with near IR (>~0.7 eV) excitation.

5. ACKNOWLEDGEMENTS

This research was supported by the Taiwan International Graduate Program of Academia Sinica, National Science Council, Ministry of Education in Taiwan, and US AFOSR-AOARD.

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