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Electron transport at InGaN/electrolyte interface and its application to water photolysis using visible light

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1. Introduction

We studied the electron transport between $In_xGa_{1-x}N$ and electrolyte solution by using cyclic voltammetry, compared with Pt, TiO_2/FTO (Fluorine-doped Tin Oxide glass). The forward and reverse reactions of $H_2 \rightleftharpoons 2H^+ + 2e^-$ occured at Pt and TiO_2/FTO electrodes. In contrast, in GaN and $In_{0.12}Ga_{0.88}N$ electrodes, only forward reaction occured and no reserve reaction of $H_2 \rightharpoonup 2H^+ + 2e^-$ was observed. These results show that GaN [1] and $In_{0.12}Ga_{0.88}N$ [2] have higher comduction band-edge potentials than the reduction potential of H^+ (aq) in water. Moreover, we observed cathodic photocurrent with p-$In_{0.12}Ga_{0.88}N$ electrode under 405nm visible light irradiation in Na_2SO_4 solution and H_2 bubbles on electrode surface were detected by monitoring the scattered light intensity.

2. Experimental

In cyclic voltammetry, the Pt, TiO_2/FTO, n-GaN, and p-$In_{0.12}Ga_{0.88}N$ were used as working electrodes. The TiO_2/FTO thin layer was fabricated by the sol-gel method. TiO_2 layer was composed of about 30nm nanocrystals. The tickness of the TiO_2 layer was about 150nm. The n-GaN and p-$In_{0.12}Ga_{0.88}N$ were grown by metal organic vapor phase epitaxy (MOVPE) on c-plane sapphire substrate. The electron concentrarion of n-GaN layer was measured as 3.9×10^{19}cm^{-3}. The Al/Au was used as ohmic electrode. The p-$In_{0.12}Ga_{0.88}N$ was grown on p-GaN/ undoped GaN/ p-InGaN sapphire substrate. The hole concentrarion of p-$In_{0.12}Ga_{0.88}N$ layer was measured as 1.2×10^{17}cm^{-3}. The as-grown sample was annealed at 600 °C in air after depositing Ni/Au as ohmic electrode.

Cyclic voltammetry and I-V characteristics in dark and under light illumination were mesured by the potensiostat, Pt counter electrode and Ag/AgCl reference electrode in 0.1 mol/l Na_2SO_4 solution (pH7). Photocurrent action spectrum was measured by irradiating monochromatized light from 100W Xe lamp. The incident photon-to-current efficiency (IPCE) was plotted as a function of wavelength of incident light.

Experiments of water photolysis and light scattering monitoring were carried out at the same time. The 405nm line from a 200W Hg-Xe lamp was used as an excitation of p-$In_{0.12}Ga_{0.88}N$. The H_2 bubbles generated from p-$In_{0.12}Ga_{0.88}N$ were identified by H_2 detector. The part of 405nm scattered light from H_2 bubbles on p-$In_{0.12}Ga_{0.88}N$ electrode surface was introduced into a photodiode array through an optical fiber.

3. Results and disucussion

Figs 1 to 4 show the cyclic voltammograms of Pt, TiO_2, n-GaN, p-$In_{0.12}Ga_{0.88}N$ in 0.1 mol/l Na_2SO_4 solution. In Figs 1 and 2, the reverse reaction of $H_2 \rightharpoonup 2H^+ + 2e^-$ occurs at -0.8V (Pt) and -1.4V (TiO_2) respectively. This is because the Fermi level of Pt and the conduction band-edge of TiO_2 are located near the reduction potential of H^+ (aq). Especially, a larger reverse reaction observe in TiO_2/FTO than Pt is probably due to the surface nanostructure of TiO_2. In Figs 3 and 4, the peak showing the reverse reaction was not observed. These results show that the conducion band-edges of GaN and $In_{0.12}Ga_{0.88}N$ are higher than the reduction potential of H^+ (aq).

Fig.5 is the photocurrent action spectra of p-$In_{0.12}Ga_{0.88}N$ showing the cathodic photocurrent, due to the electron injection from semiconductor electrode to electrolyte. The absorption edge of p-$In_{0.12}Ga_{0.88}N$ was about 430nm corresponding to the band-gap energy.

Fig.6 shows the I-V characerisitics of p-$In_{0.12}Ga_{0.88}N$ electrode in the dark and under 405nm light irradiation. Under 405nm light irradiation, the cathodic current rises at about +1.2V and the current almost consists of cathodic photocurrent up to -1.5V.

Fig.7 shows the changes of scattered light intensity from p-$In_{0.12}Ga_{0.88}N$ electrode at the constant cathodic currents of 5, 10, 15, and 30μA under 405nm light irradiation. At 5μA, the current was almost photocurrent, and a slow increase in scattered light intensity was observed. But in the current larger than 10μA, dark current was involved as shown in Fig.6. The convex upward curve is the result of superimposing the change in scatterd light intensity from various size of H_2 bubbles. The scatterd light intensity increased with cathodic current. The drop of intensity corresponds to the separaton of H_2 bubbles from surface.

4. Conclusions

It was shown that whether the reverse reaction of $H_2 \rightharpoonup 2H^+ + 2e^-$ occurs or not depends on the energy level of the conduction band-edge of semiconductor electrode. The conduction band-edges of GaN and $In_{0.12}Ga_{0.88}N$ were higher than the reduction potential of H^+, therefore, during the excitation by light, the electrons are transfered from p-GaN and p-$In_{0.12}Ga_{0.88}N$ to water to generate H_2. Experimentally, the p-$In_{0.12}Ga_{0.88}N$ electrode under 405nm visible light irradation in 0.1 mol/l Na_2SO_4 solution showed cathodic photocurrent and H_2 generation was detected by monitoring the scattered light intensity from electrode surface.

Acknowledgments

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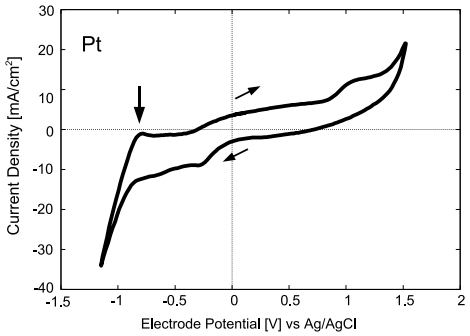

Fig.1 Cyclic voltammogram of Pt electrode in 0.1 mol/l Na_2SO_4 solution

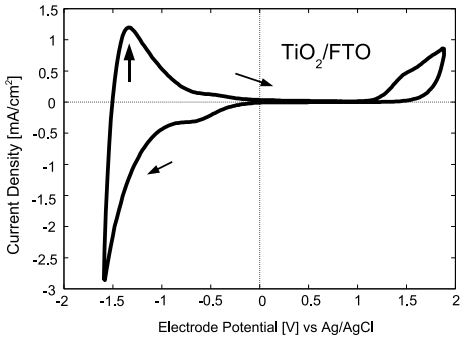

Fig.2 Cyclic voltammogram of TiO_2 electrode in 0.1 mol/l Na_2SO_4 solution

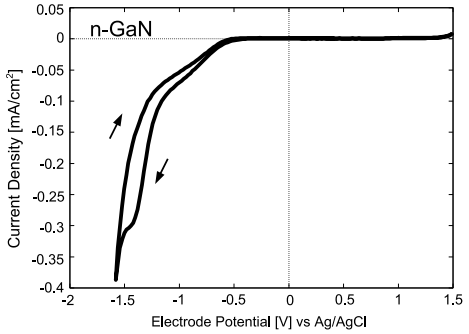

Fig.3 Cyclic voltammogram of n-GaN electrode in 0.1 mol/l Na_2SO_4 solution

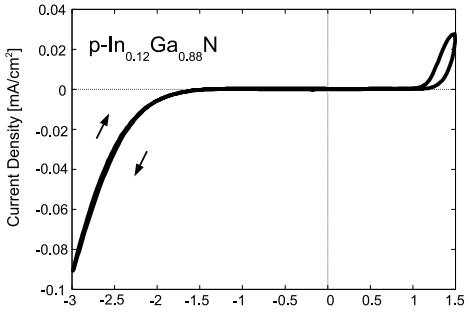

Fig.4 Cyclic voltammogram of p-$In_{0.12}Ga_{0.88}N$ electrode in 0.1 mol/l Na_2SO_4 solution

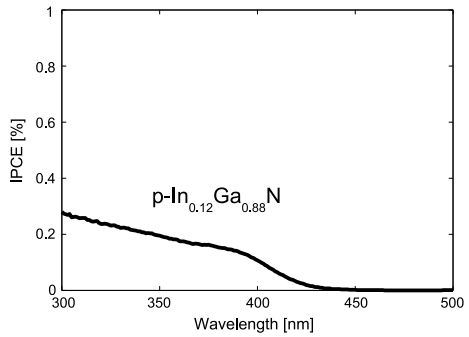

Fig.5 IPCE spectrum of p-$In_{0.12}Ga_{0.88}N$ in 0.1 mol/l Na_2SO_4 solution

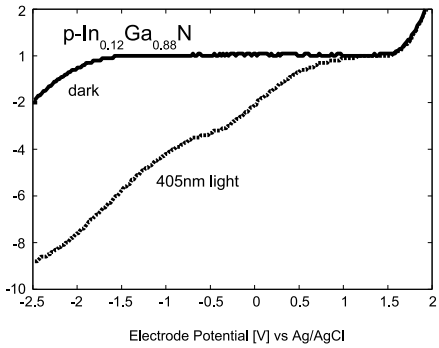

Fig.6 I-V characteristics of p-$In_{0.12}Ga_{0.88}N$ in 0.1 mol/l Na_2SO_4 solution in dark and under 405nm light irradiation

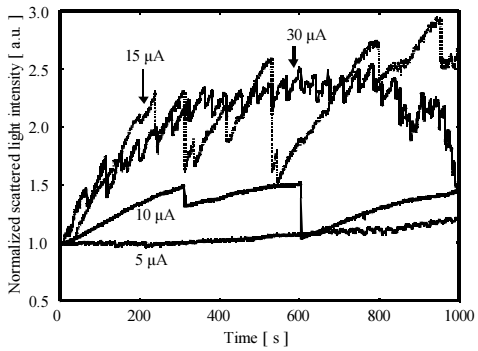

Fig.7 Scattered light intensity from p-$In_{0.12}Ga_{0.88}N$ at cathodic currents (5μA-30μA)