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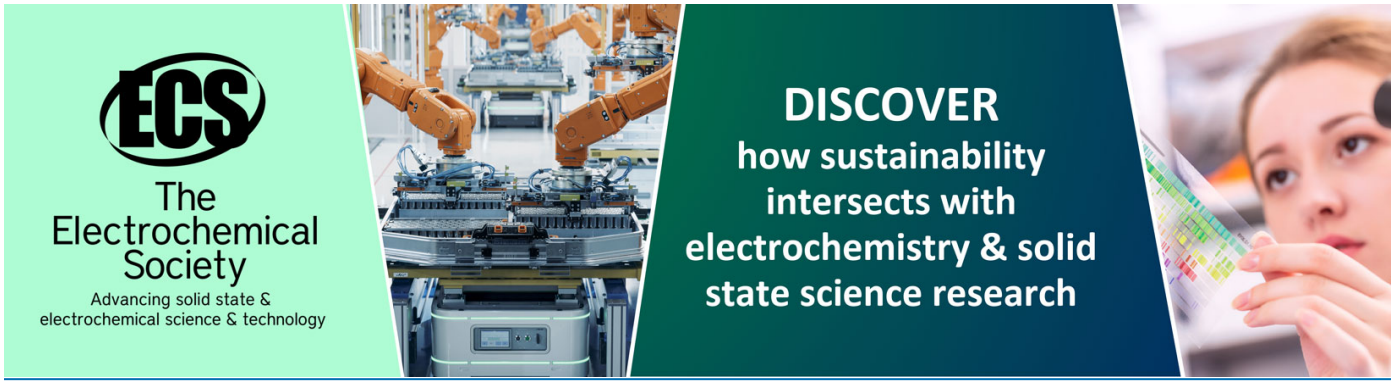

Specific of a photocurrent in GaN-based photoelectrochemical cell

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Abstract. An influence of various parameters of a photoelectrochemical cell (PECC) having a GaN working electrode on the photocurrent was studied. Type of the aqua electrolyte (alkaline (KOH)-, neutral salt (Na_2SO_4)- and acid (H_2SO_4)- based electrolytes) influences on transient time for the photocurrent stabilization. A transient time for the photo current stabilization was observed under illumination by the UV LED light sources. The shortest transient time and the highest photocurrent were observed in the alkaline-based electrolyte (~0.5M KOH) with n-GaN working electrodes (N_D-N_A =(3-5)×10^{16} cm^{-3}). PECC with electrolytes based on sodium sulfate and sulfuric acid demonstrated longer transient time (up to ten minutes) for the photocurrent stabilization and smaller photocurrent.

1. Introduction

Since the end of the 20th century, investigations to make a photoelectrochemical cell (PECC) based on wide band-gap semiconductor materials for hydrogen production under the solar illumination is still prospective and challenge topic for researchers. The reason is well known: hydrogen is considered to be a candidate as the substantial energy carrier and the Sun is an inexhaustible source of energy that provides to the Earth's surface more than 1000- 800 W/m^2 in the summer time and 500-300 W/m^2 in the winter time and water resources are enormous. GaN-based semiconductors are promising materials for not only light-emitting devices, but also for splitting water into H_2 and O_2 photoelectrochemically being immersed into an electrolyte aqua solution [1] although GaN itself can effectively absorb only the UV portion (about 5%) of the solar spectrum.

At the direct water splitting process, the GaN-based material as a photoelectrode in an aqueous solution of electrolyte may spontaneously decompose water into H_2 and O_2 gases by sunlight absorption. The sunlight absorption creates the electron-hole pairs (carriers) that being separated can participate in the gases evolution reaction at the semiconductor/electrolyte interface. However, the carrier recombination and the corrosion (or etching) of the photelectrode material substantially reduce the electron-hole pairs population and the gas production. The corrosion is an issue for n-type materials because upward band-bending at the photoelectrode/electrolyte interface promotes to separate carriers and to transfer photo-generated holes to the electrolyte. The holes not only oxidize water producing oxygen (hydrogen is produced on the counter electrode of PECC in this case) but can

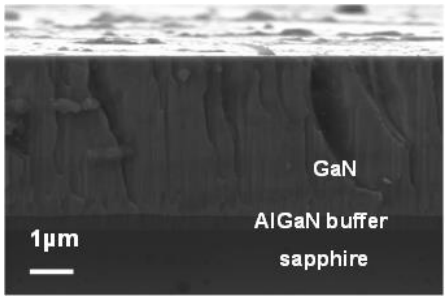
oxidize and etch the photoelectrode. This process is usually accomplished by dropping the photocurrent with time indicative non stability of the electrode. In this work we studied an influence of various parameters of PECC having a GaN layer as a working electrode on the photocurrent.

2. Experimental details

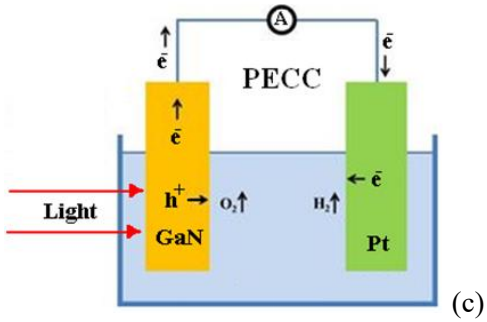
Several 5-8 μm thick GaN layers were grown by hydride vapour phase epitaxy (HVPE) on c-plane 2-inch sapphire substrates. The growth procedure included in-situ sapphire substrate treatment and an AlGaN buffer layer deposition followed by GaN layers growth. Details of the structure growth and characterization can be found elsewhere [2]. For n-GaN layers, the N_D-N_A concentration measured by C-V characterization was from of 3×10^{16} cm^{-3} to $4\times10^{18}cm^{-3}$. The N_A-N_D concentration for p-GAN layers was near $(1\text{-}2)\times10^{18}cm^{-3}$. Figure 1a shows a view of a cross section of one of the layer taken from scanning electron microscope (SEM).

To make electrodes for PECC, the intra-volume laser scribing was applied to cut 15 mm × 15 mm chips from 2-inch GaN/sapphire wafers. This scribing technique is associated with a plasma breakdown in sapphire substrate under irradiation by a short pulse of high power density laser beam [3]. The procedure did not pollute the chip surface. After that, a standard photolithography procedure was applied to deposit a 2-mm wide Ni/Au contacts on the chip edges. Figure 1b shows a view of the electrode made. The irradiated area was adjusted to 1 cm^2. The contact was protected by fluorine-based varnish to prevent its etching in the electrolyte.

A digital multi-meter and an UV-radiometer were used to measure the photocurrent and the luminous flux (the optical power of the light) of the incident light from the light sources on the GaN-electrode surface. Typically, PECC has GaN working electrode and Pt-plate as counter electrode. The parameters under consideration were (1) electrolytes based on KOH, Na_2SO_4, and H_2SO_4 water solutions with a concentration of 0.25-0.75M, (2) n-type and p-type GAN layers, and (3) three types of light sources used for samples illumination: a solar simulator (Sun Simulator Newport), a 345-nm light emitting diode (LED), and a 365-nm LED, hereinafter SSN, LED-345, and LED-365, respectively. The initial optical power of SSN, LED-345, and LED-355 was 2.5 W/m^2, 40 W/m^2, and 80 W/m^2, respectively.



(a)



(c)


(b)

Figure 1. Schematic of the photoelectrochemical cell (PECC) with GaN photoelectrode.
(a) SEM cross sectional view of GaN layer on sapphire;
(b) Top view of 15 mm×15 mm GaN photoelectrode. Irradiated area is ~1 cm^2. Contact bars on the edge is covered by fluorine-based varnish;
(c) schematic of photoelectrochemical cell.

3. Results and discussion

Figure 2 shows results of photocurrent measurements as a function of time using three light sources and KOH aqua electrolyte with concentration of 0.75M. The experiments were performed with the same sample. A position of the light sources was adjusted to have the same power of the incident light on the electrode surface of 2.5 W/m^2. Any serious corrosion of the sample surface was not observed because of the relatively low photocurrent. A transient time for the photo current stabilization was observed under illumination by the LED-based light sources. The most stable over time (although smaller in magnitude) photocurrent was measured under illumination by SSN. One of the reasons for that is the SSN has smaller intensity of the UV portion in the total spectrum than UV LED sources.

A specific band-bending at the n-GaN electrode (anode)/electrolyte interface forms the extended space charge region in the semiconductor, which separates the photo carriers and creates photocurrent. Illumination by LED-365 gave the highest photocurrent. LED-365 has relatively narrow peak emission that is pretty close to the GaN energy gap and effectively absorbs mostly on a distance from the surface lowering the carriers' recombination before they can be split by the space charge region having an associated electric field. However estimated efficiency of the process is near 0,5% or lower.

Experiments with a neutral salt (Na_2SO_4) and acid (H_2SO_4) aqua electrolytes in PECC demonstrated longer transient time (up to ten minutes) for the photocurrent stabilization and smaller photocurrent. Obviously the n-GaN electrode (anode)/electrolyte space charge region (potential barrier) depends on the electrolyte type. Narrower space charge region (lower potential barrier) results in lower photocurrent (lesser electron-hole pairs can be separated). It looks that among the neutral salt and the acid aqua electrolytes alkaline (KOH-based) electrolyte has higher barrier at the n-GaN/electrilyte interface. Further experiments were performed using KOH-based aqua electrolyte and SSN light source because of stable photocurrent.

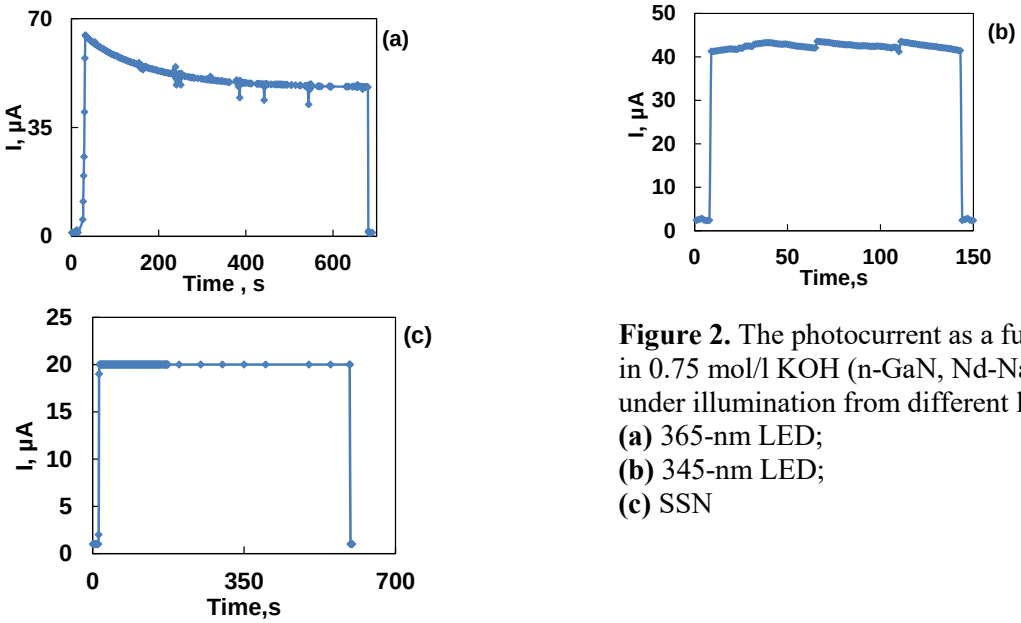


Figure 2. The photocurrent as a function of time in 0.75 mol/l KOH (n-GaN, Nd-Na~ 5×10^{16}cm^{-3}) under illumination from different light sources.
(a) 365-nm LED;
(b) 345-nm LED;
(c) SSN

Figure 3 summarizes some results of the photocurrent measurements under SSN illumination in relation with the KOH electrolyte concentration and the GaN layer doping. The max photocurrent was measured in n-GaN (N_D-N_A = (3-5)$\times10^{16}$cm^{-3}) immersed in 0.5M KOH. KOH concentration has minor effect on the photocurrent.

Note, n-GaN layer under illumination became the anode, i.e. holes generated at the surface go to the electrolyte and excited electrons go through the external surface to the Pt counter electrode. At the same conditions, p-GaN layers became the cathode with much lower photocurrent.

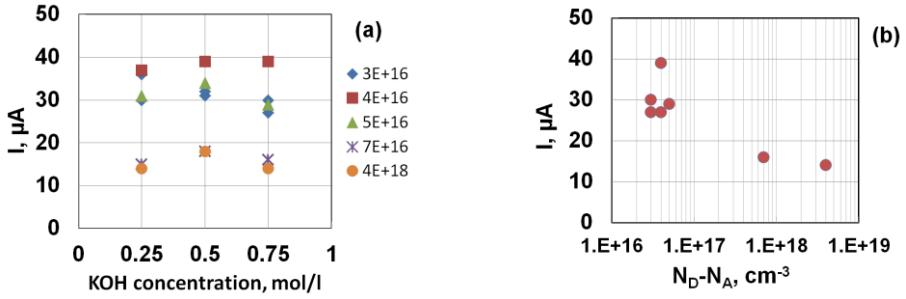


Figure 3 The influence of the electrolyte concentration and the GaN electrode doping on the photocurrent. **(a)** KOH aqua solution. Legend shows N_D-N_A concentration in GaN layers used; **(b)** N_D-N_A concentration in n-GaN layers.

4. Conclusions

Type of the aqua electrolyte (alkaline (KOH)-, neutral salt (Na_2SO_4)- and acid (H_2SO4)- based electrolytes) in PECC influences on transient time for the photocurrent stabilization. The shortest transient time and the highest photocurrent were observed in the alkaline-based electrolyte.

The max photocurrent was measured in a low-doping n-GaN layers (N_D-N_A =(3-5)×10^{16}cm-3) in 0.5M KOH. KOH concentration has minor effect on the photocurrent. n-GaN layer under illumination became the anode, i.e. holes generated at the surface go to the electrolyte and excited electrons go through the external surface to the Pt counter electrode. At the same conditions, p-GaN layers became the cathode with much lower photocurrent.

Acknowledgments

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