Testing of Stability and Spectroscopic Response of NiO(OH)/Ni$_2$Si/n$^+$/n-Si-Photoanode *

Guozheng Li and Shixun Wang

Department of Chemistry, Shandong University,
Shan Da Nan Road 27, Jinan, Shandong, P.R. China

Nikola Getoff

Institut für Theoretische Chemie und Strahlenchemie der Universität Wien, Austria

A stable multilayer n-type silicon photoanode is produced by evaporating or sputtering a thin nickel film on the silicon surface and subsequently annealing in argon atmosphere. Its properties are investigated under various conditions. Under irradiation with intense light at a constant potential, no appreciable decrease of the photocurrent was observed during a period of 100 hours, while oxygen gas was evolved. The action spectra of this photoanode, measured under different potentials, showed that its absorption extends in a broad region.

Keywords: Epitaxial silicon, Ni-modified n$^+$/n-Si, NiO(OH)/Ni$_2$Si/n$^+$/n-Si-Photoanode, Oxygen evolution.

Introduction

The most commonly used material for the production of photovoltaic converters with high efficiency is silicon. However, this well known semiconductor material with its suitable band gap ($E_G = 1.1$ eV) is unstable in aqueous electrolyte solutions. Hence, various attempts have been made in order to enhance its corrosion resistance, especially in the case of photo induced water decomposition. Nakato et al. [1] reported the effect of Pt on the surface of silicon semiconductor. Fan et al. [2, 3] investigated the same kind of modified semiconductors with respect to suppression of corrosion effects. On the other side it has been established by Rubloff [4] that thin layers of metal deposited onto silicon could react with it at relatively moderate temperatures resulting in silicides.

In order to overcome the photopassivation of silicon it is necessary not only to take care of covering the semiconductor with a thin protective film, but also to form an underlayer which is able to stabilize the substrate on the surface. In this respect, Wang et al. [5] found that by treating silicon with Ni a NiO(OH) film is formed which possesses a good transparency and is acting as an efficient photoanode for photoinduced oxygen evolution. In addition to this, Li et al. [6, 7] studied very carefully the photoelectrochemical characteristics of Ni-modified epitaxial n-Si anodes. Among other things they established that the formation of a Ni$_2$Si-layer is crucial in respect to the corrosional resistance. Further, the difference in the photocurrent density at constant potential on n$^+$/p-Si/NiO(OH) and n$^+$/n-Si/NiO(OH) anodes implies that the solid junction intensifies the separation of electron-hole pairs. This fact contributes essentially to the photoinduced oxygen evolution.

The purpose of the present work was to establish the efficiency of the spectroscopic response and to study various photoelectro-chemical characteristics, e.g. the photocurrent-light intensity dependence and the corrosion resistance of the NiO(OH)/Ni$_2$Si/n$^+$/n-Si anode during photoelectrolysis of water.

Experimental

Epitaxial silicon wafers with (111) orientation (n$^+$/n-junction depth 8–10 μm, resistivity of heavily phosphor-doped n$^+$-layer and epitaxial n-layer: 0.001 and 2.2 Ohm/cm, respectively, were obtained from Shandong University Instruments Factory. Vari-

ous procedures for preparation of the electrodes including etching, sputtering (or evaporating) and making ohmic contact were previously described [6]. The thermal treatment of the photoanodes was carried out at 350 to 650 °C in argon atmosphere for 30–60 min. Auger Electron spectra (AES) and X-ray Photon-Electron Spectra (XPS) were obtained with a spectrometer model PHI 550 ESCA/SAM. The photoelectrochemical behaviour of the modified silicon samples was studied by measuring photocurrent-scan potential curves (scan rate: 5 mV s^{-1} at a potential range of 0.20 V to 2.6 V SCE). The experimental equipment consisted of a wave-form generator, a potentiostat and an X-Y plotter. The experiments were carried out in an electrochemical cell using 1 mol dm^{-3} KOH as electrolyte. A 300 W Xenon-Lamp with water filter was used as light source, and the light beam was mechanically interrupted by a chopper. The light intensity was calibrated by means of a radiometer (Ysi-Kettering, Model 65 A). Monochromatic light was provided by a monochromator (Model S, Kratos). The photocurrent was normalized by adjusting the monochromator slit for constant intensity.
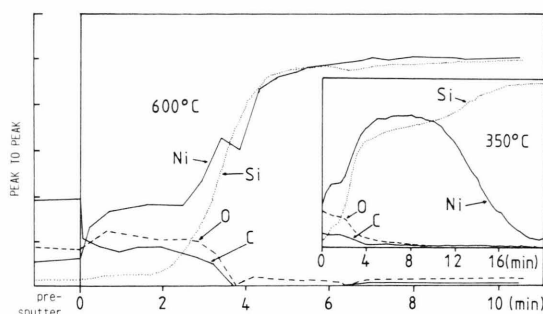

Fig. 1. Auger Electron spectrum (AES, at 3 kV, 1.3 mA) of thermally annealed Ni-modified epitaxial silicon surface at 350 °C (see insert) and 600 °C as a function of sputter time (min).
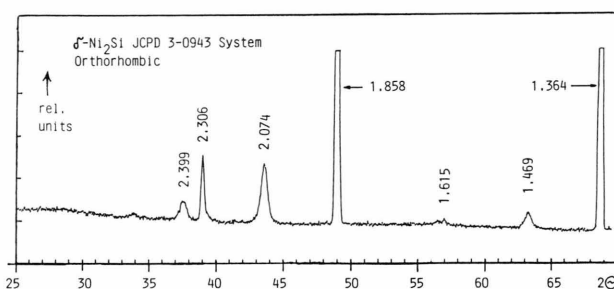

Fig. 2. X-ray diffraction of Ni-modified epitaxial silicon wafer after thermal treatment at 650 °C for 60 min in argon. The two main peaks (1.364 and 1.858) show that Ni$_2$Si compound is formed on the surface.

Results and Discussion

As previously indicated [6, 7], the thermal annealing of metal-modified epitaxial silicon is of essential importance. Fig. 1 shows depth profile diagrams of Ni-modified epitaxial silicon wafers obtained by the sputter method after annealing in argon at 350 °C and 600 °C. It seems that Ni atoms at 350 °C (insert of Fig. 1) can diffuse through the interface into the bulk upto 150 µm with about equal thickness of sputtered Ni-layer. In the mixed region, there is no sign to indicate that any nickel silicide is formed. On the other hand, by thermal annealing at 600 °C (Fig. 1) a certain portion of nickel diffuses into the bulk of silicon, and a mixed region occurs. However, it can not be precisely stated whether some kind of nickel silicide is formed or not. Obviously, from Fig. 1 it can be concluded that a NiO-film is only detected in the region where the out most layer of silicon wafers is modified.

Figure 2 shows X-ray diffraction of Ni-modified epitaxial silicon wafer after annealing at 650 °C for 60 min in argon atmosphere. The two peaks (1.858 and 1.364) express the formation of Ni$_2$Si on the sur-

face under the film of NiO (see also Fig. 1). This means that the nickel modified silicon wafer has a multiple layer structure. Based on the experimental data it can be assigned as NiO/Ni$_2$Si/n$^+$/n-Si. When this wafer is used as an electrode and is polarized anodically under illumination the NiO film in converted into NiO(OH). Hence, anodes of this type were designated as NiO(OH)/Ni$_2$Si/n$^+$/n-Si.

Photocurrent potential curves (I-V-curves) of polarized NiO(OH)/Ni$_2$Si/n$^+$/n-Si-electrode (immersed in 1 mol dm^{-3} KOH), which are obtained under illumination with pulsed white light at different intensity are shown in Figure 3.

In the course of these procedures the formation of oxygen gas was observed. The I-V-curves illustrate the effect of the adsorbed oxygen on the semiconductor surface (SCS), its partial reduction to $\dot{O}_2^-$ radical anion and reoxydation to O$_2$ [8–10]. The main possible reactions responsible for the O$_2$-formation using a
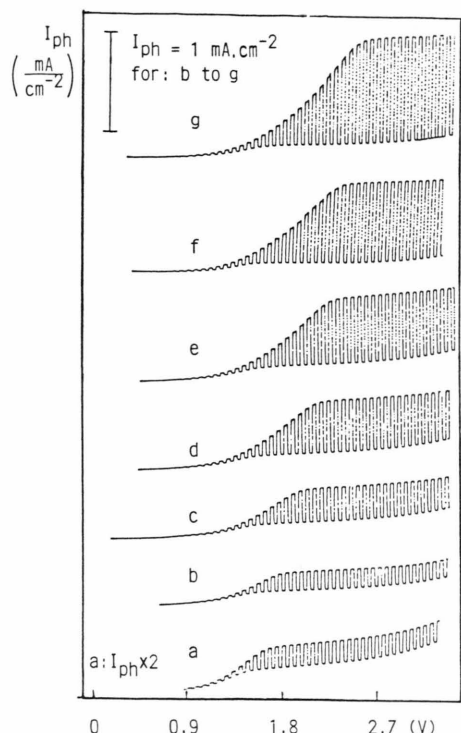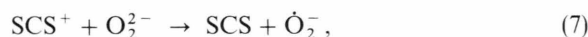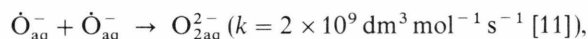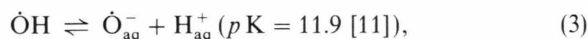
Fig. 3. Photocurrent (I_{ph} in mA cm^{-2}) of NiO(OH)/Ni$_2$Si/n$^+$/n-Si-photoanode as a function of the applied potential (V vs SCE) at various light intensities (mW cm^{-2}): (a) 0.141, (b) 0.25, (c) 0.44, (d) 0.68, (e) 0.86, (f) 1.06 and (g) 1.38. – Scan rate: 5 mV s^{-1}. – Light pulse = dark time – 1 s. – Electrolyte: 1 mol dm^{-3} KOH.
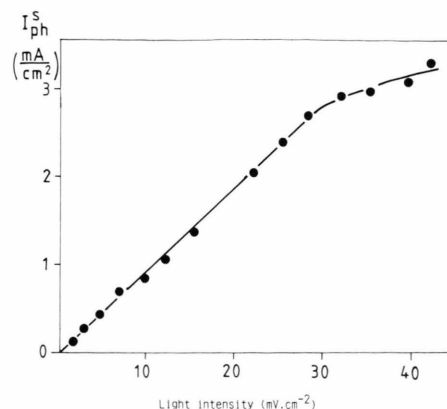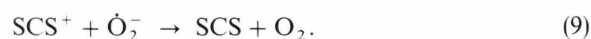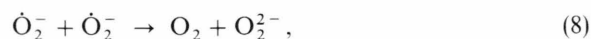

Fig. 4. Saturation photocurrent density (I_{ph}^s in mA cm^{-2}) as a function of the light intensity (I_L, mW cm^{-2}) of NiO(OH)/Ni$_2$Si/n$^+$/n-Si-photoanode. – Light source: 300 W Xenon lamp with water filter.

Further, the formation of ozonide (O_3^-) as transient species near the SCS is also possible, which can be subsequently reduced on the SCS$^+$ resulting in O$_2$ and O-atoms.

It might be mentioned that the O-atoms are rather strong corrosion agents. However, even by applying a scan potential over 4 V (vs. SCE) no passivation of the photoanode was observed. This fact demonstrates, that the NiO(OH)/Ni$_2$Si/n$^+$/n-Si is a quite corrosion resistant photoanode.

From Fig. 3 one can obtain the saturation photocurrent density as a function of the intensity of white light as shown in Figure 4. In the range of a light intensity upto about 30 mW cm^{-2} the relationship between saturation current density and intensity is practically linear. It is further to be mentioned that the photocurrent at a constant potential, e.g. 1.8 V, is observed as a linear function at lower intensity. Increasing the light intensity above 30 mW cm^{-2}, the curve is tending to reach a plateau, which can be attributed to the photosaturation phenomenon.

Figure 5 (I) shows the action spectra of photocurrents at various anodically applied potentials without keeping the light intensity constant. The very good light absorbability in the wide wavelength range from 480 to 800 nm shows that the NiO(OH) film with band gap of $E_g \simeq 2.3$ eV can also absorb light of short wavelengths, whereas silicon is absorbing light of long wavelength near its band gap of 1.1 eV. with regard to the linear relationship between extremely low light intensity and photocurrent, one can obtain the nor-

basic electrolyte are taking place on or near the SCS:

$$SCS \xrightarrow{h\nu} (SCS^+ e^-) \rightarrow SCS^+ + e^- \text{ (to cathode),} \quad (1)$$

$$SCS^+ + OH^- \rightarrow SCS + \dot{O}H, \quad (2)$$

$$\dot{O}H \rightleftharpoons \dot{O}_{aq}^- + H_{aq}^+ (pK = 11.9 \text{ [11]}), \quad (3)$$

$$SCS^+ + \dot{O}_{aq}^- \rightarrow SCS + \dot{O}, \quad (4)$$

$$2\dot{O} \rightarrow O_2, \quad (5)$$

$$\dot{O}_{aq}^- + \dot{O}_{aq}^- \rightarrow O_{2aq}^{2-} (k = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ [11]}), \quad (6)$$

$$SCS^+ + O_2^{2-} \rightarrow SCS + \dot{O}_2^-, \quad (7)$$

The peroxy-radicals ($\dot{O}_2^-$) appearing as intermediates (having $pK = 4.8$ [12]: $\dot{O}_2^- + H^+ \rightleftharpoons H\dot{O}_2^-$) can disproportionate to oxygen and dissociated peroxide or/and react with SCS$^+$:

$$\dot{O}_2^- + \dot{O}_2^- \rightarrow O_2 + O_2^{2-}, \quad (8)$$

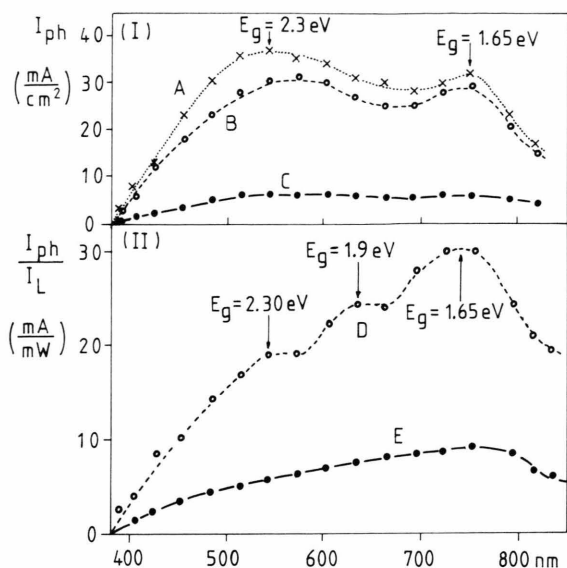$$SCS^+ + \dot{O}_2^- \rightarrow SCS + O_2. \quad (9)$$

Fig. 5. Photocurrent spectra (I_{ph}) of NiO(OH)/Ni$_2$Si/n$^+$/n-Si-anode using 1 mol dm^{-3} KOH as electrolyte at different potentials. (I) unnormalized photocurrent density (I_{ph}) as a function of λ (nm) at 2 V (A), 1.5 V (B) and 1 V (C). (II) normalized I_{ph} vs. λ (nm) using 2 V (D) and 1 V (E).
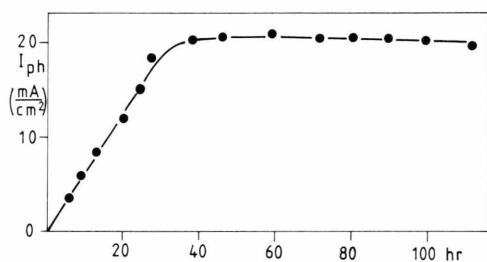

Fig. 6. Photocurrent density (I_{ph}, mA cm^{-2}) of NiO(OH)/Ni$_2$Si/n$^+$/n-Si-anode measured at a potential of 1 V as a function of time (hr). – Electrolyte: 1 mol dm^{-3} KOH. – Light source: 150 W Bromine-Tungsten lamp with water filter.

Fig. 7. Photocurrent (I_{ph}, mA) of NiO(OH)/Ni$_2$Si/n$^+$/n-Si-photoanode produced by pulsed white light as a function of time (s) at constant potential (vs SCE): (A) 1.40 V, (B) 1.80 V, (C) 2.20 V and (D) 2.40 V. – Electrolyte: 1 mol dm^{-3} KOH. – Light source: 300 W Xe-lamp. – Light pulse = dark time = 3 s. – Maximum current value (I_{ph}, mA) of: (A) 0.775, (B) 1,72, (C) 2.50 and (D) 2.76.

malized photoresponse by dividing the photocurrent density (I_{ph}) by the monochromatic light intensity (I_L in mW cm^{-2}). Figure 5 (II) shows normalized photocurrent spectra for two different applied potentials. At a constant voltage of 2.0 V, the spectrum shows two absorption shoulders (at ∼ 550 nm and ∼ 640 nm) and an absorption maximum at 740 nm, which might correspond to the three layers of the photoanode. The spectrum also indicates that the multiple layer NiO(OH)/Ni$_2$Si/n$^+$/n-Si photoanode has a light absorbability in a wide wavelength range.
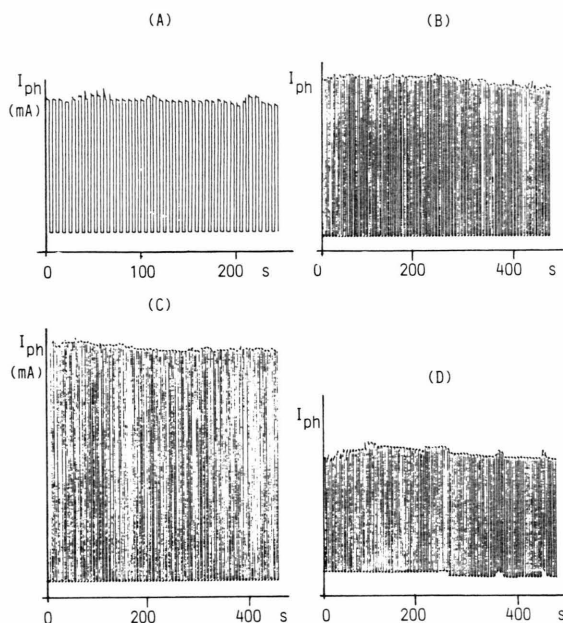
At a constant potential lower than 1.0 V, its efficiency is rather low.

In Fig. 6 the photocurrent density (I_{ph}; mA/cm^2) of the NiO(OH)/Ni$_2$Si/n$^+$/n-Si-anode is presented as a function of long operation time. During the first 40 hr of anode operation the NiO-layer on the surface is changed to NiO(OH) as established by X-ray diffraction measurements. After that the current remains rather unchanged upto 100 hr. The photocurrent of the photoanode is also fairly stable in respect to pulsed light. This behaviour is demonstrated by using the intermitting light source at various applied potentials. From the data presented in Fig. 7 (inserts A, B, C, and D) it is obvious that even at different supporting voltage the corresponding photocurrent remains rather constant. This fact illustrates the good stability of the photoanode.

The photoanode of NiO(OH)/Ni$_2$Si/n$^+$/n-Si multilayers operated for 100 to 150 hr in 1 mol dm^{-3} KOH solution is also checked in respect to its chemical stability and corrosion resistance by X-ray diffraction measurements. The obtained results indicate that the

Ni$_2$Si layer becomes gradually amorphours NiO(OH), whereby the minority of photogenerated holes is scavenged by Si, and hence, as shown in Fig. 6, the photocurrent density for oxygen revolution slowly decreases.

Further investigations are in progress in order to improve the efficiency of photoanodes of this type.

Conclusion

Sputtered or vacuum evaporated Ni-films on the surface of n$^+$/n-Si semiconductor can diffuse into the bulk of silicon and form Ni$_2$Si under thermal annealing in argon atmosphere at elevated temperature, e.g. 650 °C. Under operation in aqueous electrolyte of 1 mol dm^{-3} KOH a multi layer NiO(OH)/ni$_2$Si/n$^+$/n-Si photoanode is established, which possesses an absorption spectrum from 450–800 nm. Thereby three absorption regions are observed, which very likely correspond to the existence of three semiconductor layers. The formation of Ni$_2$Si facilitates the stabilization of the photoanode. After long term anodic polarisation under illumination this layer is transformed into an NiO(OH)-amorphours film with rather high corrosion resistance and photoefficiency.

[1] Y. Nakato, M. Hiramoto, Y. Iwakabe and H. Tsubomura, J. Electrochem. Soc. **132**, No 3, 330 (1985).
[2] F.-R. F. Fan and G. A. Bard, J. Electrochem. Soc. **129**, 1647 (1982).
[3] F.-R. F. Fan, G. Keil, and A. J. Bard, J. Amer. Chem. Soc. **105**, 324 (1983).
[4] J. Rubloff, Surf. Sci. **132**, 268 (1983).
[5] Shixun Wang, Guozheng Li, and Guoxian Xu, Acta Physiochim. Sinica **1**, 104 (1985).
[6] Guozheng Li and Shixun Wang, J. Electroanal. Chem. **227**, 213 (1987).
[7] Guozheng Li, Shixun Wang, Jingeng Chen, Xinghua Luo, and Nikola Getoff, XIIth Intern. conf. on Photochemistry, Budapest, Hungary, Abstracts **II**, 484 (1987).

[8] K. J. Hartig and N. Getoff, p. 81–96, Vol. 1 in "Hydrogen Systems", Eds. T. N. Veziroglu, Zhu Yajie, and Bao Deyou, China Acad. Publ., Beijing and Pergamon Press, Oxford 1985.
[9] K. J. Hartig and N. Getoff, Int. J. Hydrogen Energy **11**, 773 (1986).
[10] A. Schwarz, K. J. Hartig, and N. Getoff, in "Hydrogen Energy Progress VI", Proceed. 6th WHEC, Vienna, Austria, July 1986; Eds. T. N. Veziroglu, N. Getoff, and P. Weinzierl, **2**, 643 (1986).
[11] L. M. Dorfman and G. E. Adams, "Reactivity of Hydroxyl Radical in Aqueous Solutions", ed. by National Bureau of Standards, Washington, D. C., (1973).
[12] N. Getoff and M. Prucha, Z. Naturforsch. **38a**, 589 (1983).