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POROUS SILICON SCHOTTKY-TYPE HYDROGEN SENSORS AND CELLS

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Electrical and capacitance characteristics of Schottky-type Au/Porous Si (Au/PS) structures have been investigated. Generation of electricity (the open-circuit voltage and short-circuit current) and capacitance up to 550 mV, 25 mA/cm^2 and 600 nF, respectively, on placing Au/PS structures in $NaBH_4$ was discovered. This effect is mainly caused by hydrogen component of $NaBH_4$. The possible mechanism related with hydrogen-stimulated generation of voltage and capacitance in Au/PS interface is suggested.

Keywords: Porous Silicon, Hydrogen, Sodium Borohydride, Sensor, Cell

INTRODUCTION

The structure of porous silicon (PS) is characterized by a high internal surface area, which for PS wafer with dimensions of 1cm x1cm x10μm is about of 500cm^2. PS surface is covered by silicon hydrides and silicon oxides, and that is highly reactive in elevated temperatures. Surface bonds, in particular Si-H bonds play an important role in regulating electrical, optical, luminescence and other properties due to the large internal surface area of PS. The porosity of structure opens new perspectives for using PS-based structures as gas sensors. Numerous gas and humidity sensors based on PS have been presented [1-6]. Principle of work the most gas sensors consists in change of resistivity or capacitance of the material or structure. It is obviously that work of such resistive or capacitive type sensors demands to apply of electricity from external source. The operation of new type humid and gas sensors on base of Schottky-type metal/PS structures investigated in [7-11] do not demand applying of electricity. On the contrary, such structures in humid or gas ambient produce electricity. By other words, metal/PS structures working on humidity (gas) – voltaic effect discover both the gas sensor and gas cell properties.

In this paper we present data on change of electrical and capacitance characteristics of metal/PS Schottky-type structures in $NaBH_4$ solution. Generation of voltage, current and capacitance in metal/PS structures on dipping in sodium borohydride solution was discovered.

EXPERIMENTAL

The PS layers on Si substrates were prepared by anodic etching in HF:H_2O solution at a dc current of about 15 mA/cm^2 under white illumination [11]. n-type Si (111) monocrystalline wafers of resistivity $\rho = 1x10^{-2}$ Ω cm are used as substrates. PS layers of thickness 10-20 μm, average porosity of 60- 80% and resistivity of about 2 x 10^6 Ω cm were analysed in this work. Au-PS-Si structures have been fabricated by evaporation of Au film (100-200 nm) onto the PS surface at room temperature using the electron-beam evaporation technique. *In* or *In-Ga* alloy was used as Ohmic contact to PS layers. The I-V characteristics, open-circuit voltage (V_{oc}), short-circuit current (I_{sc}) and capacitance between contacts to Au film and PS layer of Au/PS Schottky-type structures were measured at normal room conditions (300K, 45%RH) and in $NaBH_4$:H_2O solution. Conductivity of sodium borohydride solution was measured by using '3200 Conductivity Instrument' (YSI). Concentration of conducting hydrogen ions (protons) in solution from conductivity measuring is calculated using equation [12]

$$\sigma=(F^2/RT)D_pN_p \qquad (1)$$

Here F is Faraday's constant ($9.65x10^4$ C), R is gas constant (8.31 J/mol.K), T is absolute temperature, D_p is diffusion coefficient of protons and N_p is protons concentration.

RESULTS AND DISCUSSION

The I-V characteristics of Au/PS structure in normal air ambient and in $NaBH_4$ solution showed the good rectifying properties (Fig.1). Herewith the values of current under 'reverse' voltage (the 'negative' polarity on Au film) the stronger degree rise (about of 115 times) on dipping in $NaBH_4$ solution as compared with the reverse current in air, whereas current for the 'forward' voltage in $NaBH_4$ increases by factor 3 as compared with forward current in air. Measuring of I-V characteristics of Au/PS structures in dark, day-light and under a tungsten-halogen lamp illumination showed that they are weakly sensitive to illumination.

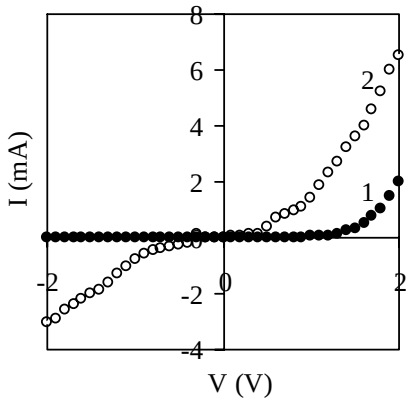

Figure 1. I-V characteristics of Au/PS structure (1) at room conditions (T=300K, 45%RH) and (2) in $NaBH_4$ solution.

The effect, similar to humidity-voltaic effect [7-11], i.e. generation a voltage between the contacts to Au film and PS layer under humidity exposition, was also discovered on dipping of Au/PS structure into $NaBH_4$ solution. Figure 2 illustrates the open-circuit voltage arising in Au/PS structure dependent on the concentration of $NaBH_4$ solution (N). It is seen that the V – N dependence have view of curve with maximum (V =500 mV) at N = 30 mg/ml. In the range of concentration of $NaBH_4$ solution up to 30mg/ml gradient of curve (dV/dN) is large (about of 13 mV.ml/mg), i.e. voltage generated in Au/Ps structure is very sensitive to $NaBH_4$ concentration. It should be noted that the Au/Ps structure on dipping into $NaBH_4$ solution also exhibits the short-circuit current (about of 25 mA/cm^2).

The capacitance generated in Au/PS structure in $NaBH_4$ solution depending on the solution concentration was shown in Fig. 3. It can be seen in Fig. 3 that C-N dependence, similarly V-N curve (Fig. 2) shows the maximum value of capacitance (C =1000 nF) for $NaBH_4$ solution with N=30 mg/ml.

Figure 4 shows the response-recovery behavior of the short-circuit current for Au/PS sensor on the successive cycles placing in normal room atmosphere and in $NaBH_4$ solution (N=30 mg/ml). It is seen that the response time is about of 20-30 s. Moreover, the amperometric response of Au/PS structure shows almost same current (about of 120 μA) for 60 min. It is be noted that the response-recovery curve for open-circuit voltage of Au/PS structure (V-t) on successive cycles of placing in air and $NaBH_4$ solution is similar to the I-t dependence presented in Fig. 4.

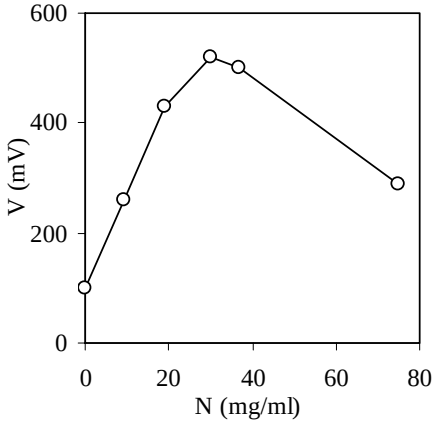

Figure 2. Voltage generation in Au/PS structure as a function of the $NaBH_4$ contents in $NaBH_4$-H_2O solution.

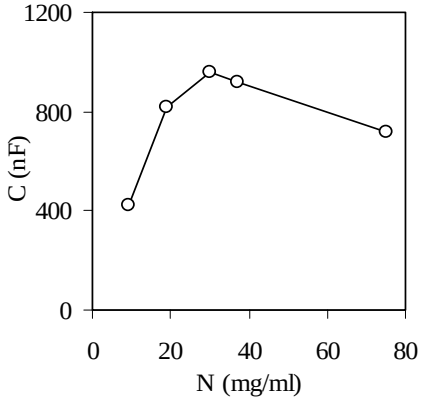

Figure 3. Capacitance generation in Au/PS structure as a function of the $NaBH_4$ contents in $NaBH_4$-H_2O solution.

Figure 5 illustrates the response-recovery of capacitance for Au/PS sensor at successive putting in air and $NaBH_4$ solution. Here, as in Fig. 4 the capacitance forming in placing in $NaBH_4$ solution was found to be stable (about of 580 nF) for 60 min and response time is about of 20-30 s.

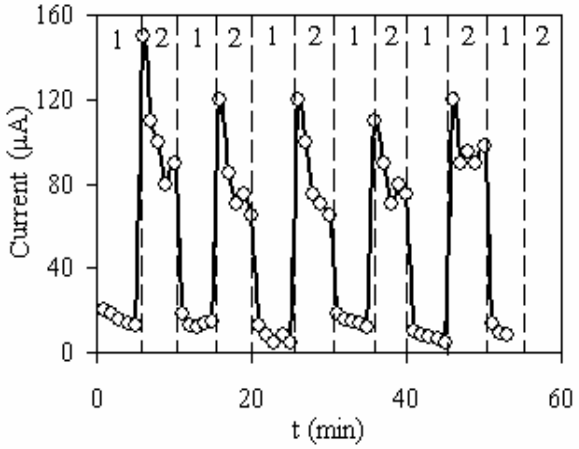

Figure 4. Current response of Au/PS structure as a function of storage time on the successive placing in (1) air and (2) $NaBH_4$ solution (30mg/ml).

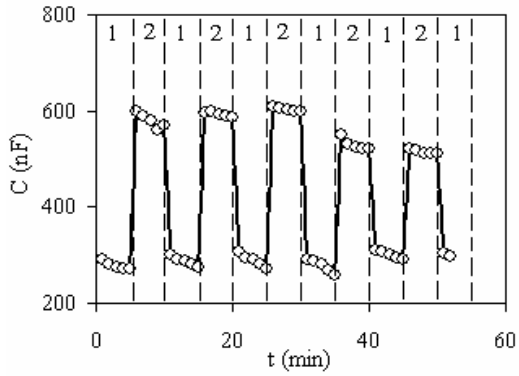

Figure 5. Capacitance response of Au/PS structure as a function of storage time on the successive placing in (1) air and (2) $NaBH_4$ solution (30mg/ml).

The dependence of the solution conductivity on $NaBH_4$ contents is presented in Fig. 6. As can be seen from this figure, the conductivity increases with increasing $NaBH_4$ contents. This effect can be caused by hydrogen production from $NaBH_4$ in water [13]

$$NaBH_4 + H_2O \rightarrow aBO_2 + 4H_2 \qquad (2)$$

This reaction takes place at 45°C in the presence of catalyst. One can suppose that part of hydrogen molecules at room temperature can split with formation of protons ($H_2 \rightarrow 2H^+ + 2e^-$), which can be responsible for increase of conductivity of the solution. Calculation of proton concentration in $NaBH_4$ solution with N = 400 mg/ml (Fig.6) using Eq. (1) gives $N_p = 6x10^{11}$ cm^{-3}.

Thus, the next experimental facts related with change of electrical and capacitance characteristics of Au/PS Schottky-type structure in placing in $NaBH_4$ are established:

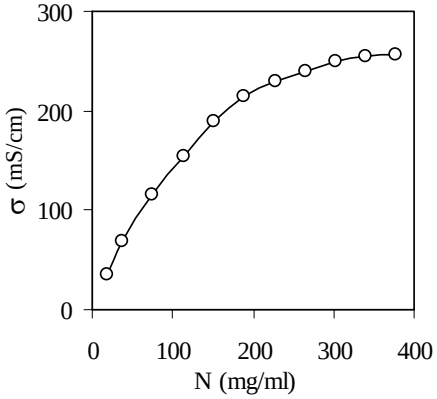

Figure 6. Conductivity of $NaBH_4$-H_2O solution as a function of $NaBH_4$ contents.

1) Placing of Au/PS structures in $NaBH_4$ solution results in the increasing of both forward and reverse currents, herein the increasing for the reverse currents is stronger than that for the forward bias.
2) Formation of the open-circuit voltage, short-circuit current and capacitance was observed for structures placed in $NaBH_4$ solution.
3) Values of V_{oc}, I_{sc} and C depend on $NaBH_4$ contents in the solution.
4) This phenomenon is reversible, i.e. placing and removal of Au/PS structure from $NaBH_4$ solution is accompanied by response and recovery of these parameters, respectively.

The mechanism of generation of electricity in metal/PS cells under humid exposition proposed in [7-11], can be also applied for explanation of generation of electricity in hydrogen-containing $NaBH_4$ solution. In Au/PS structures, the Au film on the PS plays role of catalyst. H_2 molecules in $NaBH_4$ solution, settled on a surfaces of catalyst, are split on hydrogen ions (protons) and electrons. Then, protons diffuse through Au film to metal-PS interface, that results in introducing dipoles at Au-PS interface, whereby an induced voltage across the dipoles. The V-N dependence observed in Fig.2 can be explained by two concurrent phenomenon. On the one hand, for the relative low contents of $NaBH_4$ (N<30 mg/ml) increase of $NaBH_4$ concentration in solution accompanied by increasing of proton concentration (up to $2x10^{11}$ cm^{-3}) results in rising of voltage. On the other hand, at large contents of $NaBH_4$ (N>30 mg/ml), productions of reaction (2) precipitate in pores of Au and porous silicon and thereby hindering penetration protons to interface. Concerning the increase of both reverse and forward currents of I-V characteristics in $NaBH_4$ solution (Fig.1), this effect may be attributed to additional ionization of hydrogen atoms in the electrical field of Schottky-type junctions accompanied by an increase the number of charge carriers. Mechanism arising of capacitance can be related with change of dielectric constant of PS in $NaBH_4$ solution due to interaction of protons with pore surfaces.

Thus, Schottky-type Au/PS structures sank in hydrogen-containing NaBH4 solution generate voltage up to 550 mV and capacitance up to 1000 nF. These data indicate on perspectivity of using Au/PS structures as both hydrogen cells and sensors.

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