

## Porous Silicon-Based Hydrogen Detectors

T.D. Dzhabarov<sup>1,2</sup>, C. Oruc<sup>1</sup>, S. Aydin<sup>1</sup>, E.Cingi<sup>1</sup>, D.Oren<sup>1</sup>

<sup>1</sup>Department of Physics, Yildiz Technical University, Davutpasa, 34210 Istanbul, Turkey

<sup>2</sup>Institute of Physics, Azerbaijan National Academy of Sciences, 370143 Baku, Azerbaijan

**Abstract** In this work the humidity-voltaic effect, i.e. generation of open-circuit voltage ( $V_{oc}$ ) in metal (Cu, Ag, Au)-Porous silicon structures under humid exposition is discovered. Besides, influence of porosity of free-standing PS and humidity on optical and electrical properties of films were investigated.

Relatively to the optical and electrical properties of free-standing PS films the next main results were received. (a) The rising of film porosity (from 30% to 90%) results in both the increase of band gap of PS films (from 1.4 to 1.9 eV) and resistivity (from  $2 \times 10^4$  to  $4 \times 10^4 \Omega \text{ cm}$ ), (b) The resistivity of films along pores approximately two tenth as large as than that in across direction, (c) The band gap of films in humid ambient in the range of 55-95 %RH increases from 1.6 to 1.8 eV. The observed porosity-stimulated and humidity-stimulated changes optical and electrical characteristics were interpreted on the base model including the quantum confinement of charge carries in the PS microcrystallites and chemical activity of PS surfaces.

Formation of open-circuit voltage up to 450mV, 280mV and 200mV for Au-PS, Cu-PS and Ag-PS structures under humidity or hydrogen exposition is observed. It is suggested that the humidity-voltaic effect, i.e. generation of  $V_{oc}$  in humid atmosphere is mainly caused by splitting of water and hydrogen molecules on surfaces of Ag, Cu or Au catalyst and hydrogen diffusion from humid ambient to metal-PS interface. Approximately the linear increase of  $V_{oc}$  depending on the average porosity of PS films is established. Generation of  $V_{oc}$  (up to 550 mV) have been also observed on dipping of Au-PS structures in different hydrogen-containing solutions (ethanol, benzine, sodium tetraborate pentahydrate etc.). These results open the perspective for using of metal-PS structures as both gas (hydrogen) detectors and mini hydrogen cells.

### 1. Introduction

The discovery of visible photoluminescence from porous silicon (PS) has attracted considerable interest due to its potential application in the development of silicon-based optoelectronic devices. However, the origin of photoluminescence in PS is still controversial. A few models are suggested for explanation mechanism of photoluminescence. According model proposed by Canham [1] radiative recombination of electron-hole pairs occurs within nanometer silicon wires and their energy gaps become larger than that of bulk Si (quantum confinement effect). This model modified by Koch et al. [2] suggests that electron-hole pairs are photo-excited in nanometer silicon particles and radiatively recombined via Si intrinsic surface states. Another model [3] suggests that luminescence from PS was caused by some special luminescence materials, such as  $\text{SiH}_x$  complexes, polysilanes, or  $\text{SiO}_2$  rather than an intrinsic property of nanometer Si. A third model believes that excitation of charge carriers occurs in nanometer silicon particles and the photoexcited carriers transfer into the luminescence centers (defects and impurities) in the surrounding  $\text{SiO}_x$  layers [4].

In general, main models proposed for explaining the origin and mechanism of visible photoluminescence in PS can be divided on three groups. The first group comprises an intrinsic effects in nanometer Si, whereas the second group of model is related with processes proceeding an external surfaces of nanocrystals, i.e. on surfaces of PS. These processes are determined with composition and structure of materials on PS surfaces. The third group combines models of the first and second group. The structure of PS is characterised by an extremely large surface area to volume ratio (up to  $10^3 \text{ m}^2 \text{ cm}^{-3}$ ). It is known that surface bonds, in particular Si-H and Si-O bonds play an important role in regulating of

electrical, optical, luminescence and gas sensing properties of PS. These properties of PS are very sensitive to humidity of ambient. Investigations of optical properties of the free-standing PS films can promote understanding mechanism of photoluminescence. The optical and electrical characteristics of free-standing films depending on porosity are rarely considered [5]. Xu et al. [6] have measured evolution of the optical absorption of free-standing PS films during thermal oxidation in air and decreasing of the gap have explained due to the Si-O bond formation. Sagnes et al. [7] have measured the absorption spectra of the free-standing PS films with porosities in a range of 45-79 % and observed a blue-shift of curves with an increase of the porosity. As far as our knowledge goes, data on effect of humidity on optical absorption spectra of free-standing PS films are absent in literature.

It is noting that the gaseous environment exerts influence on electrical and photoluminescence characteristics of PS and metal-PS structures. The composition and optical property changes of PS caused by hydrogen and oxygen diffusion are considered [8,11]. Numerous gas and humidity sensors based on PS have been presented [12,13]. Humidity-stimulated changes of I-V characteristics and generation of open-circuit voltage in Ag-PS and Cu-PS Schottky-type structures have been observed [14,15]. These changes are attributed to penetration of hydrogen from humid ambient and diffusion via porous silicon surfaces to metal-PS interfaces. It will be noted that the response and recovery time of PS based gas sensors is limited by diffusion coefficient of gas atoms and molecules along inner PS surfaces. Therefore knowledge of diffusion parameters of atoms influencing on gas-sensing characteristics of PS is very important for fabrication of gas sensors with the low response and recovery times.

In this work the optical and electrical properties of free-standing PS films in dependency on porosity and humid exposition were investigated. Humidity (hydrogen)-stimulated open-circuit voltage generation in metal (Au, Ag, Cu)-PS structures is discovered and mechanism of this phenomenon was discussed. Besides data on diffusion coefficient of hydrogen on PS surfaces, determining the response characteristics of gas sensors were determined.

## 2. Experimental Procedure

PS films were formed by anodization of (111)-oriented n-type silicon wafers (0.01  $\Omega$ .cm) in HF-ethanol solution at constant current density under the white light illumination. The PS films were then detached from the Si substrates by electropolishing [8]. The free-standing PS films were characterized by porosity, thickness, resistivity and optical measurements. Free-standing PS films of thickness 5-20  $\mu$ m and porosities of P= 30-90 % were analysed in this work.

The transmission spectra of free-standing PS films were measured from 300 to 1000 nm at room temperature by using 'UV/VIS Lambda 2S' (Perkin Elmer) spectrometer. Resistivity measurements were performed along and across of pores. Optical and electrical measurements of PS films were examined on the normal room conditions (T=300 K, 40 %RH) and in the measuring cell at different ambient humidity (water vapour) in the range of 40-95 %RH. The relative humidity (RH) in cell was measured by using 'Extech-444701' Hygro-Thermometer.

This investigation focuses on the analysis the transmission spectra and resistivity in dependency on both porosity of PS films (for normal room conditions) and relative humidity of ambient (for PS films with given porosity). Time-dependence transmission spectra and resistivity under humidity exposition in cell were measured after successive 5- or 10-min cycles of humid exposition.

The absorption coefficient ( $\alpha$ ) is deduced from transmission spectra by solving  $\alpha$  in the equation [8]

$$T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \quad (1)$$

Here  $R$  is reflectivity and  $d$  is the effective sample thickness.

The next values  $n=1.42$  and  $R=0.03$  were received for the refractive index and the reflectivity from experimentally measured the interference spectrum of free-standing PS film. This value of the refractive index is close to  $n=1.33$  measured in [7].

Metal-PS structures and Au-PS-Si structures have been fabricated by evaporation of Au, Ag or Cu film onto the PS surface at room temperature using electron-beam evaporation technique. The thickness of metal film (80-160 nm) was measured during evaporation by using ‘Deposition Controller’ (Inficon, Leybold). In or In/Ga alloy was used as ohmic contact to PS layers. The current-voltage characteristics, humid-stimulated voltage generation in metal-PS structures were examined in the measuring cell at different ambient humidity (water vapour, hydrogen or oxygen). Humidity-stimulated voltage ( $V_{oc}$ ) between the open contacts to metal film and PS under gas exposition (moisture, hydrogen or oxygen) or on dipping of metal-PS structure in hydrogen-containing solution (ethanol, benzene, sodium tetraborate pentahydrate etc) is directly measured using ‘Thurlby’ 1503 Digital Multimeter.

The photosensitive properties of metal-PS structures were analysed by measurements of current-voltage characteristics in dark, day-light and under illumination by a tungsten-halogen lamp ( $150 \text{ mW/cm}^2$ ). All investigated structures showed very slight photosensitiveness. Value of the open-circuit photovoltage in day-light and under tungsten-halogen lamp illumination was about of 1-3 mV. Therefore most of humidity-sensitive measurements have been performed at day-light illumination.

### 3. Results and Discussion

Measuring of transmission spectra at room conditions ( $T=300 \text{ K}$ ,  $40 \text{ \%RH}$ ) was carried out for free-standing PS films with porosity of 46%. Fig. 1 shows the absorption coefficient spectrum for PS film with thickness of  $8 \mu\text{m}$  and porosity of 46%. Analysis of measured curves of absorption coefficient ( $\alpha$ ) versus photon energy ( $h\nu$ ) for PS films with porosity in range of 30-90 % showed that spectra displayed behavior expected for the direct semiconductors

$$\alpha^2(h\nu)^2 = A(h\nu - E_g) \quad (2)$$

Here  $E_g$  is energy gap and  $A$  is constant. Absorption coefficient curves for PS films discovered a continuous blue-shift with increase of porosity in range of 30-90 %.

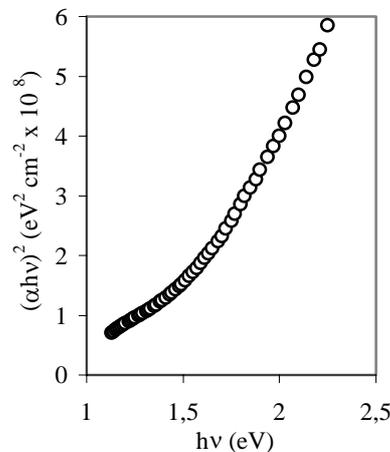


Figure 1. Optical absorption spectrum of PS film of  $P= 46 \text{ \%}$  porosity ( $40 \text{ \%RH}$ ).

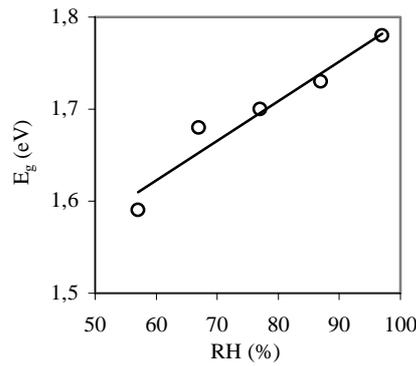


Figure 2. Energy gap of PS films in dependency on porosity (40 %RH).

Fig. 2 shows the energy gap in dependency on porosity of the free-standing PS films, determined from extrapolation of high energy part of ( $\alpha - hv$ ) spectra. Near linear increase of band gap from 1.4 to 1.9 eV with rising of porosity of PS films in the range of 30-90 % is observed.

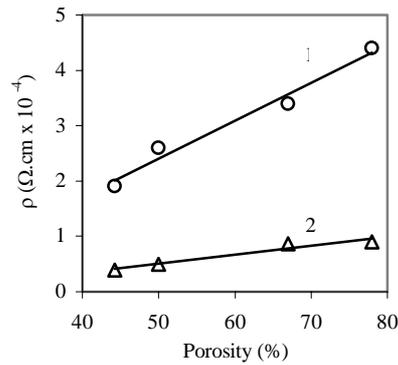


Figure 3. Resistivity of PS films (1) along and (2) across of pores (40 %RH).

Fig. 3 presents resistivity along and across of pores for free-standing PS films with porosity in a range of 45-78 %. Increase of resistivity with increase of porosity is observed for both directions. The data on resistivity - porosity dependence (Fig. 3) correlate with increase of energy band gap of PS films with rising in porosity (Fig. 2). Lower low values of resistivity across of pores can be related with presence of low-porosity layer along PS film - Si substrate interface.

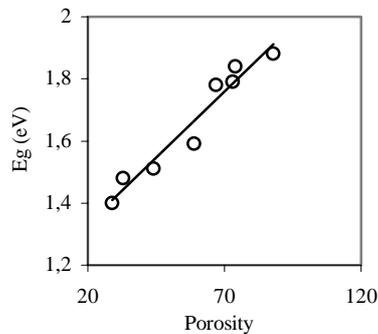


Figure 4. Energy gap of PS film in dependency on relative humidity (P=68 %).

Fig. 4 presents the energy band gap of PS films (with porosity of 68%) in dependency on relative humidity. These data were received from optical transmission measurements carried out after exposition of PS film in humid ambient for 30 min. As it is seen from Fig. 6,  $E_g$  – RH dependence, similarly energy gap versus relative humidity curve (Fig. 2), shows nearly linear increasing of energy gap.

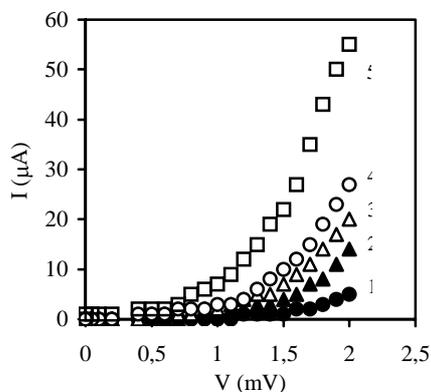


Figure 5. Reverse I-V characteristics of Au-PS structure in humid ambient (1) 45 %RH, (2) 70 % RH, (3) 83 % RH, (4) 90 %RH and (5) 99 % R H (T=300K).

Data on Fig. 2 and Fig. 4 concerning increase of the energy gap in dependency on porosity of PS films and humidity respectively, can be explained by a model including the quantum confinement of carriers in the PS microcrystallites and the formation of the Si-H bonds on pore surfaces in humid atmosphere.

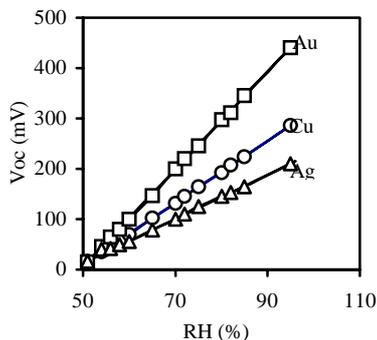


Figure 6. The open-circuit voltage - relative humidity dependence for Au-PS, Cu-PS and Ag-PS structures (T=300K).

Below it is presented data on humidity-sensitive properties of metal-PS structures.

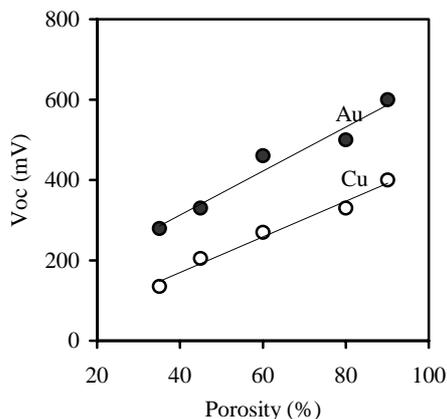


Figure 7. The open-circuit voltage versus the porosity of porous silicon (90%RH).

The typical reverse I-V characteristics of Au-PS structure in air ambient at 45 %RH, 70 %RH, 83 %RH, 90 %RH and 99 %RH at room temperature are presented in Fig. 5. Increase of reverse currents with rising of the relative humidity have been observed. The value of the current at 90 %RH (for 2V) increases in comparison with that at 45 %RH (for 2V) by factor 12.

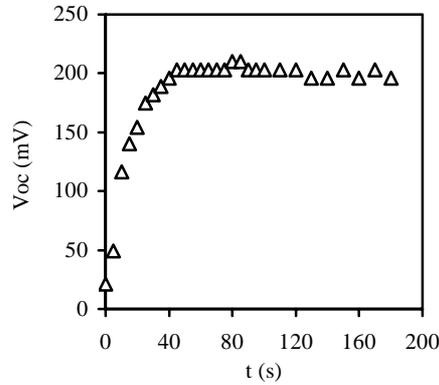


Figure 8. The open-circuit voltage in dependency on duration of exposition in humid ambient (70 % RH) for Au-PS structure (323 K).

The humidity-voltaic effect i.e. generation of a voltage between contacts to metal film and PS layer under humidity exposition is discovered for metal-PS structures. Fig. 6 illustrates the open-circuit voltage in dependency on the relative humidity for one of such Au-PS structures. It is seen that the  $V_{oc}$  approximately linearly increases from 15 mV to 450 mV with rise of the relative humidity from 51 %RH to 95 %RH. The humidity-sensitivity of Au-PS structure estimated from curve of Fig. 6 is about 10 mV/(%RH). Data on formation of  $V_{oc}$  in humid for Cu-PS and Ag-PS structures have been also presented in Fig. 6 [14,15]. Increasing of  $V_{oc}$  for Ag-PS, Cu-PS and Au-PS Schottky-type junctions (200, 280 and 450 mV respectively) correlates with values of work function of Ag, Cu and Au (4.4, 4.6 and 4.8 eV respectively).

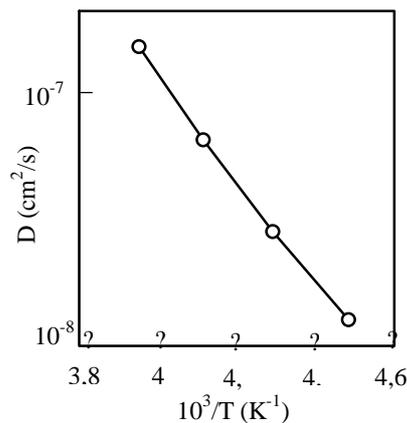


Figure 9. The temperature dependence of the effective diffusion coefficient of hydrogen in PS (for 70 %RH).

Formation of the open-circuit voltage in Au-PS structures is not observed under pure oxygen gas exposition. Contrary to oxygen, exposition under pure hydrogen gas (about of 0.5 atm) results in generation of open-circuit voltage ( up to 490 mV). These results suggest that the humidity-stimulated

formation of the open-circuit voltage is mainly caused by hydrogen component of water molecules. It will be noted that generation of the open-circuit voltage have been also observed on dipping of Au-PS junctions in different hydrogen-containing solutions (440 mV for ethanol (C<sub>2</sub>H<sub>5</sub>OH), 500 mV for benzene (C<sub>5</sub>H<sub>12</sub> – C<sub>16</sub>H<sub>34</sub>), 550mV for sodium tetraborate pentahydrate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 5H<sub>2</sub>O) etc).

Data on generation of open-circuit voltage in Au-PS and Cu-PS structures with different porosity in humid ambient (90%RH) were presented in Fig. 7. For both structures nearly linear rising of V<sub>oc</sub> (up to 600 mV for Au-PS structure) with increase of porosity was observed. Herewith values of V<sub>oc</sub> for Au-PS structure are more than those for Cu-PS structures.

It will be noted that the response time i.e. duration of reaching of the most value of V<sub>oc</sub> after placing of Au-PS structure in humid atmosphere depends on temperature. For example, data on influence of exposition duration in humid air atmosphere (70 %RH, T=323 K) on the open-circuit voltage of Au-PS structure are presented in Fig. 8. An increase of temperature from 323K to 353K is accompanied by decrease of response time of Au-PS structure from about 2 min to 40 s.

For Au-PS structures just as Ag-PS and Cu-PS structures [14,15] we suppose the next model of humidity-stimulated diffusion of hydrogen and generation of the open-circuit voltage. Before discussion of V<sub>oc</sub> generation mechanism we consider briefly the peculiarities of Au-PS structure forming by electron-beam evaporation of Au on PS layer. Gold atoms deposit primarily on external surface of PS layer at the initial stage of evaporation. Herewith the high-speed gold atoms penetrate also in pores with deposition predominantly onto bottom of pores and formation the numerous inner Au-PS junctions [16]. Then, as Au film thickness on external surface of PS layer increases, pores are fully closed by Au film. For this two-step model of formation of Au-PS structure, Au film on the external surface of PS layer plays role of catalytic membrane layer which splits water and hydrogen molecules and transmits small hydrogen atoms or ions (protons). If hydrogen is accepted as a donor impurity in PS [17], then adsorption and dissolution of the water molecules on surface of Au film due to interaction with the Au surface, subsequent penetration of hydrogen ions (protons) through Au film, diffusion via inner pore surfaces and reaching the Au-PS interfaces is accompanied by separation of charges and origin of the open-circuit voltage across Au-PS interfaces.

Data on V<sub>oc</sub> - RH dependence (Fig. 6) shows that value of the open-circuit voltage is determined by quantity of water molecules in air ambient i.e. by quantity of hydrogen. Other than for given RH the velocity of V<sub>oc</sub> rising on Au-PS Schottky-type barriers (Fig. 9) is determined by diffusion coefficient of hydrogen via inner porous silicon surfaces. On fulfilling these conditions the effective diffusion coefficient of hydrogen on PS surfaces may be estimated from V<sub>oc</sub> - t curve [9,15]. Data on the effective diffusion coefficient of hydrogen along PS surfaces for temperature range of 323-353 K for 70 %RH were presented in Fig.9. The temperature dependence of the effective diffusion coefficient of hydrogen on the PS surfaces is described as

$$D = 1.3 \times 10^{-2} \exp\left(-\frac{0.25}{kT}\right) \quad (3)$$

One can conclude that the activation energy (0.25 eV) finding in this work is rather related with the energy necessary for diffusion of hydrogen via a net of Si-H bonds on PS surfaces. There is reason to believe that hydrogen in Si-H bonds is not electrically active state. On splitting of Si-H bonds, hydrogen migrates across PS surfaces as H<sup>+</sup> ions (protons) with further trapping in Si-H bonds. Herewith the diffusion process of hydrogen across PS surfaces consists of series of successive three-step acts (splitting of Si-H bonds, migration of hydrogen ions on PS surfaces and trapping of hydrogen by Si-H bonds). To put the other way round, activation energy determined in this work is rather related with the energy necessary for splitting of Si-H bonds and migration of hydrogen across PS surfaces.

#### 4. Conclusion

It is shown that the band gap of free-standing PS films increases from 1.2 to 1.9 eV with rising porosity (from 30 to 90%), that is attributed to quantum effect arisen at special confinement of charge carries in nanometers-size crystallites and chemical activity of PS surfaces.

The generation of the open-circuit voltage in metal-PS interfaces in humid atmosphere is discovered. Comparative data on values of open-circuit voltages forming in Au-PS (450mV), Cu-PS (280mV) and Ag-PS (200mV) Schottky-type junctions correlate with work functions of Au, Cu and Ag metals. The humidity sensivity of Au-PS structures is about 10mV/(%RH). It is supposed that humidity-stimulated generation of  $V_{oc}$  is mainly caused by hydrogen diffusion from metal surface to metal-PS interface.

The effective diffusion coefficient of hydrogen via pore surfaces of PS (for 70%RH) in the range of 323-353 K increases from  $2.9 \times 10^{-8}$  to  $1.3 \times 10^{-7}$  cm<sup>2</sup>/s. Generation of  $V_{oc}$  ( up to 550 mV) have been also observed on dipping of Au-PS structures in different hydrogen-containing solutions (ethanol, benzene, sodium tetraborate pentahydrate etc). Data of this work indicate on possibility for using metal-PS structures as both gas (hydrogen) sensors and mini hydrogen cells.

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