Contributed paper

OPTO-ELECTRONICS REVIEW **13**(1), 35–38

Novel gas sensor based on porous silicon measured by photovoltage, photoluminescence, and admittance spectroscopy

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Porous silicon (PSi) layer as gas sensor, based on the change in photoconductivity, photoluminescence and admittance has been presented. PSi layer was prepared by electrochemical dissolution of p-type silicon wafer in HF. Photovoltage curves, photoluminescence spectra (PL) and admittance spectra have been measured in different gas concentrations. Photoconductivity (PC) spectra in vacuum and different gas atmosphere have been compared. Changes of photovoltage intensity curves and change of PC spectra versus concentration of vapour have been observed.

Keywords: porous silicon, gas sensor, photocurrent.

1. Introduction

Crystalline silicon (c-Si) is widely applied for production of electronic components, but it is useless for the fabrication of light-emitting devices, because silicon is a semiconductor with an indirect bandgap. It caused that radiative band to band recombination of an electron-hole par involves a phonon and is therefore a relatively slow process [1]. Consequence of this is very weak photoluminescence from silicon crystalline, even at low temperature. Therefore PSi has attracted great deal of interest due to efficient room-temperature visible photoluminescence, which for the first time was observed by Canham in 1990 [2]. Although first PSi layers had been observed by Ulrich in 1956 and later by Turner only Canham report about room temperature luminescence beginning significant interest in this material [1]. Lower cost of a product, possibility of improved performance and optical properties caused that the investigations of luminescence and electrical properties have been made in many laboratories. Researches have showed that porous silicon has attracted new optoelectronic materials. From the practical point of view, studying these structures is very important because of their wide range of applications such as photovoltaic devices [3], photodetectors [4], and light emitting diodes. Porous silicon has been very attractive material for production of gas sensor because of its extremely large surface [5]. PSi structure has been taken as matrix for immobilization of a variety of biomolecular complexes, DNA fragments, and antibodies [6]. Knowledge of admittance, PC and PL spectra is very important to develop optoelectronic devices.

In this paper we present photovoltage curves, PL spectra and admittance spectra which were measured in vacuum and in different gas concentrations.

2. Experimental

The PSi samples were produced by electrochemical anodisation of boron-doped p-type c-Si wafers. As an electrolyte the HF acid diluted in isopropyl alcohol and current density of 10 mA/cm^2 were used in this method. For photoconductivity and admittance measurements, the aluminium contacts on the PSi surface were deposited by thermally evaporation method.

Schematic diagram of PC experimental setup is presented in Fig. 1. The photoconductivity spectra have been performed using the monochromator (Zeiss SPM 2) with 250 W halogen lamp. The output light was chopped with frequency 80 Hz and duration of light on the sample surface was 2.2 ms in each cycle. The sample was put in cryostat and illuminated in wavelength range of 500–1200 nm in vacuum and different concentrations of alcohol vapour. The exit slit of the monochromator and cryostat was coupled to optical waveguide. The electrical field was applied to the sample in the forward direction (2 V). Before the photoconductivity measurements ethanol vapours were delivered to cryostat by batcher. Time-decays of photoconductivity were amplified and registered by digital oscilloscope (LeCroy 9370). Photovoltage curves were measured at a room temperature.

Photoluminescence (PL) experiments were carried out at a room temperature by excitation the samples with a pulse nitrogen laser λ = 337.1 nm, FWHM = 5 ns, power in pulse 20 kW. Intensity of laser illumination was strongly decreased by slit and glass filter. The proper band of emis-

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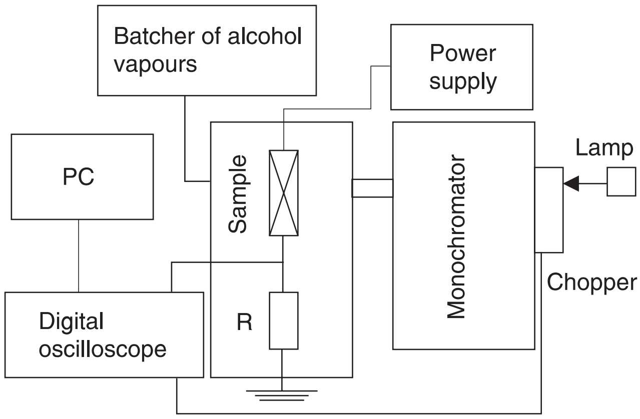

Fig. 1. Schematic diagram of PC experimental setup.

sion was selected by a monochromator (SPM-2 ZEISS) and registered by a combination of photomultiplier (R-928 HAMAMATSU) and boxcar averager (162/164 PAR). The signal was processed and analysed by a personal computer. Each sample was wet by ethanol and PL spectra were measured for every 15 minutes. After ~24 hours, the samples were enclosed in the vacuum chamber and after next 30 minutes in vacuum exposure, the last PL spectrum has been registered.

The admittance spectroscopy (AS) measurements were performed in the frequency range from 0 Hz to 250 kHz by using a DSP Lock-in amplifier EG&G 7260. The sample was located in vacuum environment and polarized with DC voltage equal to 2 V. Additionally, the sample was stimulated by a small sine signal with 200 mV amplitude. The conductance versus frequency (G-f) and capacitance versus frequency (C-f) were measured four times for different concentration of alcohol vapour. Each measurement was persisting about an hour. Frequency was changed every 25 seconds. During measurements sample was illuminated by light with wavelength equal 650 nm selected by nomochromator. The 250W halogen lamp was used as a light source. All the admittance measurements were realized at room temperature.

3. Results and discussion

Figure 2 shows photovoltage curves at selected concentrations of ethanol vapour and in vacuum under a constant applied voltage of 2 V. Wavelength of excitation was equal 900 nm. It has been observed high sensitivity of PSi structure. An increase in photovoltage can be seen even at low concentration of vapour. The considerable increase in photovoltage has been observed for high concentration of ethanol vapour. Figure 3 shows dependence of sensitivity of PSi sample on ethanol vapour concentration at excitation wavelength 900 nm that was obtained from photovoltage curves. High sensitivity for exposure to ethanol vapour above 2.5 mg/cm^3 was observed. Photoconductivity spectra at selected concentration ethanol vapour and in vacuum were calculated using collection of photovoltage curves and are presented in Fig. 4. The highest sensitivity was observed for illumination at photon energy of about 1.3 eV. For this photon energy photovoltage in vacuum has maximum intensity. Low sensitivity was observed for illumination at photon energy above 1.7 eV, even at high ethanol vapour concentration. The vapour sensitivity in the PSi structure may be explained as adsorption molecules of ethanol on the surface. Molecules on the surface induce an increase in the capacitance in Al/PSi contact by an increased permittivity [7]. Besides, ethanol molecules act as accep-

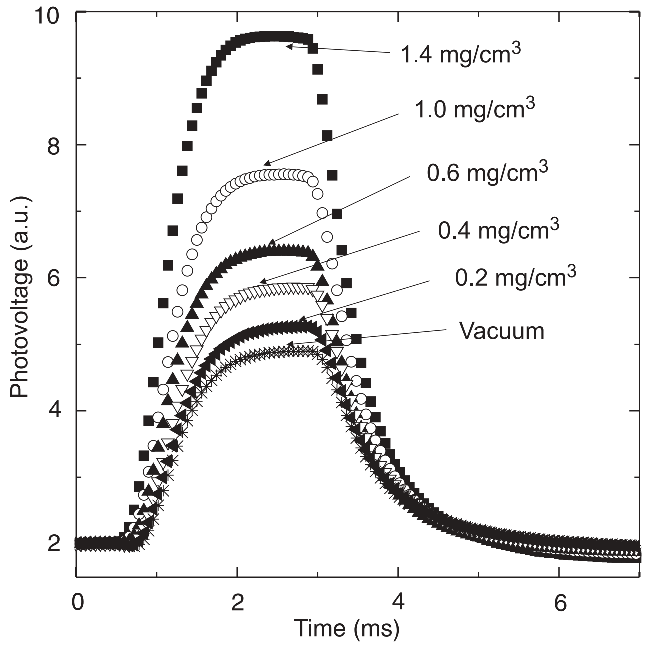

Fig. 2. Photovoltage curves at different concentration of vapour.

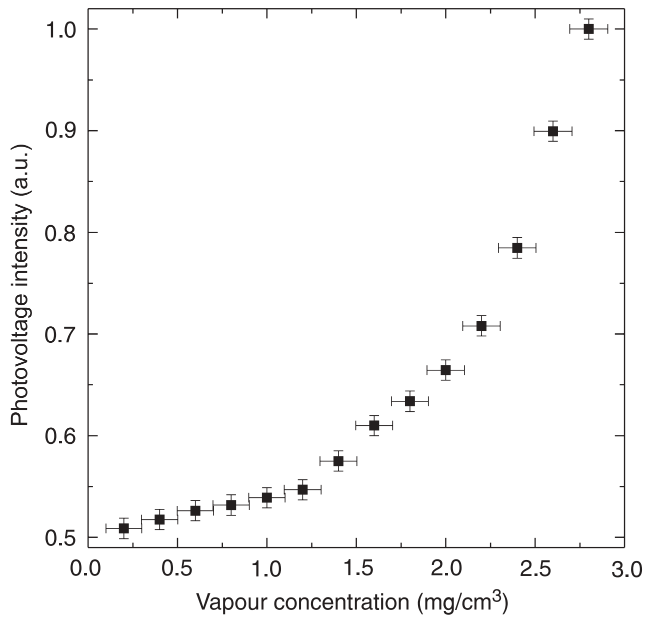

Fig. 3. Dependence of sensitivity on ethanol vapour concentration.

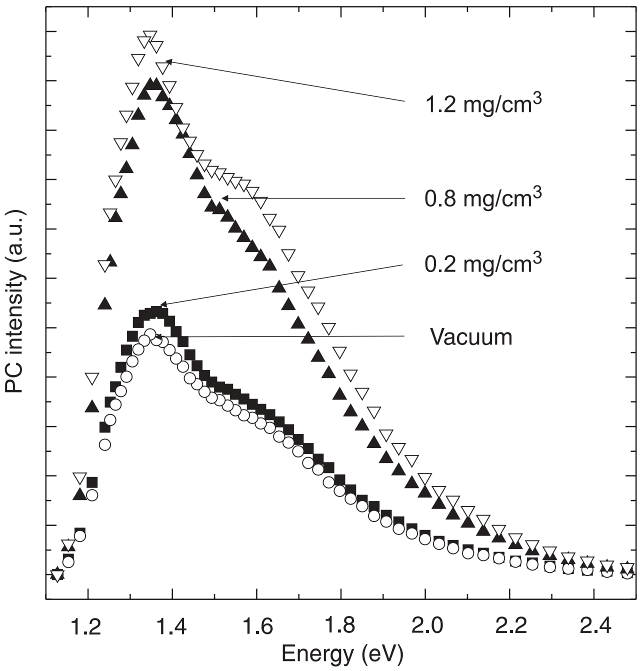

Fig. 4. Photoconductivity spectra at different vapour concentration and vacuum.

tor centres that would lead to increase in free carrier concentration and would reduce energy barrier between regions of silicon skeleton, which differ from value bandgap energy each other, in particular between crystallites or crystallite and quantum wire. Thus can be explained the increase in photovoltage.

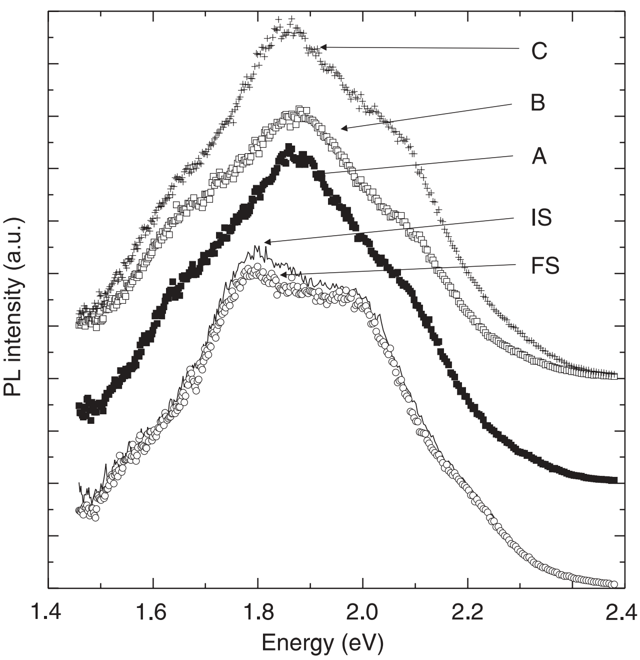

Fig. 5. Photoluminescence spectra of porous silicon sample measured on the air after exposure to ethanol: 1 min. (A), 1 h (B), 24 h (C) together with initial PL spectrum (IS) and those at the end of experiment after 30 min in vacuum (FS – final PL spectrum).

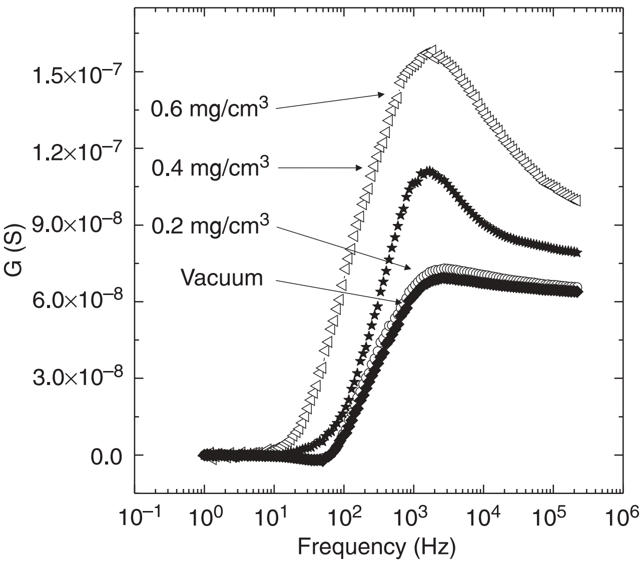

Fig. 6. Conductance of PS/c-Si structure as a function of frequency.

Figure 5 illustrates stability of the PL spectrum shape in the time after wet sample with ethanol then expose to the air. Changes of PL structure may be easy observed and they are relatively stable in time. Only partial PL recovery is observed after 24 h (C). Full recovery of spectrum shape can be done by exposure sample to vacuum environment (FS – final PL spectrum). We conclude that no irreversible displacement reactions have occurred at the surface and surface traps are only temporarily (but stable) affected.

Results of admittance measurements are presented in Figs. 6 and 7. With increase in ethanol vapour concentration we observed increase in capacitance at low frequencies and decreasing capacitance for above 1 kHz. This effect can be caused by change of speed carriers with applied of voltage. In this case, some traps are not filled and change the sign for opposite one.

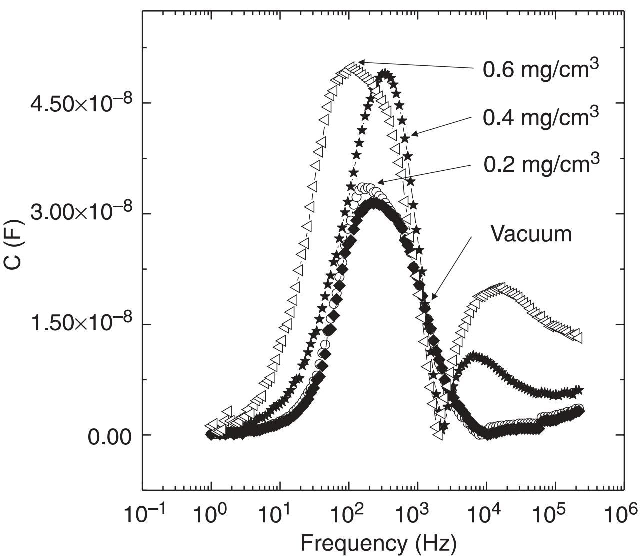

Fig. 7. Capacitance of PS/c-Si structure as a function of frequency.

4. Conclusions

PSi structure with aluminium contacts on the surface was used as a sensor. It is demonstrated that PSi structure can be used for ethanol vapour sensing at a room temperature. Large increase in photovoltage response is observed for exposure to high concentration of ethanol vapour. Changes of photovoltage curves at different vapour concentration have been observed. High sensitivity of PSi on ethanol vapour concentration have been observed for illumination at photon energy of about 1.3 eV. The response time of several seconds depends on porosity of PSi samples. For vapour concentration above 4 mg/cm^3 increase of photovoltage has not been observed. It has been demonstrated that PL spectra changes under influence exposure to ethanol vapour. Stability of this evolution of PL spectra was observed and changes of PL spectrum are near perfectly reversible. Influence of vapour adsorption on the large surface of PSi has been suggested. The mechanism of reduce of energy barrier between crystallites or crystallite and quantum wire was proposed.

Acknowledgements

This work has been supported by the University N. Copernicus Research Program (project UMK 443-F).

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