SnO/POROUS SILICON HETEROSTRUCTURE BASED HUMIDITY SENSOR

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A nanoparticle metal oxide SnO thin film fabricated on porous silicon (PS) is studied as a subject for room temperature humidity sensing device application. The structural, photoluminescence, optical and electrical properties of thin films and SnO/PS/Si heterostructures are studied. Current-voltage characteristics of SnO/PS/Si heterojunctions are measured under normal atmosphere and humid environment in the range of 62-95% RH. The humidity-resistance effect, i.e. decrease of resistance between contacts to SnO and Si substrate under humidity exposition is obtained for SnO/PS/Si heterostructures at room temperature. The structure shows well pronounced response-recovery behavior (response time about 1 min) after successive cycles of placing in humid environment. The similar dependence is observed for the capacitance under humidity. The mechanism for the humidity-stimulated electricity in SnO/PS/Si sensor at room temperature is discussed.

1. INTRODUCTION

Porous silicon (PS) has attracted attention due to wide variety of possibilities for environmental monitoring, clinical diagnostics, homeland security, automotive, photo-electronics and other applications [1-3]. Interest of porous silicon materials is very intestive in the recent years due its potential applications and gas sensors, in various areas such as air-quality monitoring, fuel cells, biomedical sciences chemical industries etc. Effect of humidity on electrical properties, optical and photoluminescence spectra of free standing porous silicon and PS samples have been studied [4,5].

The crystalline structure of porous silicon presents a network of silicon in nano (micro)-regions with an extremely large surface-to-volume ratio (up to 800 m^2/cm^3). The structure of porous silicon is like a sponge or columnar where quantum confinement effect play fundamental role. The pore surfaces are covered by silicon hydrides (Si-H) and silicon oxides (Si-O). Existence of pores, especially the canal-form pores, which determine ion (proton) conductivity along opens new perspectives for using porous silicon-structures as gas sensors. PS is characterized also by high chemical activity of the surface. These properties enable PS to effectively react with gases and PS layers are therefore considered as very promising for gas sensor applications.

Gas sensors are divided to next main categories: resistive, capacitive, solid electrolyte, infrared and other. The resistive sensors are created on the basis of tin oxide (SnO_2) or similar metal oxide semiconductors (CuO, ZnO, TiO_2 etc.). The working principle of this type sensor is that the resistance of metal oxide semiconductor changes when it is exposed to the ambient gas, i.e. gas reacts with the heated metal oxide surface and changes its electronic properties. One limitation of metal oxide gas sensors, however, is their operation temperature (350-500°C) must be lead to high power consumption.

Humidity of porous silicon sensons princile, mechanim, fabrication technologies were examined in [6]. New type of sensors for humidity and hydrogen based on metal (Ag, Au, Cu)/PS Schotky structures has been proposed in [7-10]. Metal/PS Schotky-type structures operating as humidity-sensitive sensors or sensors sensitive to hydrogen-containing gases do not need to operate under an external voltage bias. Instead, such structures in humid or hydrogen-containing atmospheres produce electricity by themselves. In other words, metal/PS structures exhibit the properties of both a gas sensor and a hydrogen fuel cell.

The sensitivity behaviors of the Au/n-SnO_2/p-PSi/c-Si sensors to H_2 and CO_2 gases were achieved sensitivity, accordingly about 60% and 95% at temperature 250-300°C [11]. Pt-catalysed SnO_2/Porous-silicon hybrid sensor of CO increased by a factor of 7.5 compared to the ones on for 10 min and c-Si (at 100°C) [12]. Influene of the deposition temperature on Ammonia gas sensing of SnO_2/Porous silicon stucture investigated and sensing characteristics depicted at the room temperature and quick response and recovery times at the deposition temperature of 350°C [13]. SnO_2-based sensors has received attention in the field of toxic gas detection due to their high sensitivity, fast response and logn-term stadibity [14]. Synthesis of ZnO-SnO_2 nano-thin films on porous silicon or glass as NH_3 gas sensing conducted in [15]. The prepared gas sensors of mixed ZnO-$Sn0_2$ give a highest sensing response for 63 ppm NH_3 on glass substrate at 200°C. The sensitivity of the prepared on the glass is better than on porous silicon.

Significant sensing response of SnO_2/porous silicon heterojunctions could be obtained at sufficiently high temperature [11-13]. The crystallic (for example, lattice constants (a, c)), and electronic structures of SnO and SnO_2 are significantly different [16].

To the best of our knowledge, the data on properties of the SnO/Porous silicon-based sensors is lacking in literature. In this study, the humidity sensing of SnO/PS/Si heterojunction has been studied and the

effectiveness of the SnO/PS/Si-based sensing device has been shown.

2. EXPERIMENTAL PROCEDURE

Monocrystalline p-type boron-doped silicon wafers with of orientation of (100), resistivity about of 10 Ω cm and thickness of about 200 μm were used for fabrication of SnO/PS/Si heterojunctions. The electrical contacts were made by screen-printed with a Du Ponta photovoltaic silver paste for front and silver with 3% aluminum paste for the back contact. Samples with silver contact baked at 200°C for 10 min. and metallization was carried out at 800°C for 10 min. in the conventional annealing furnace [9,10].

Porous silicon layers with of 10-20 μm an average porosity of 47-80 % were prepared on p-type Si substrates by anodic etching in HF:H_2O = 1:3 solution at a *dc* current of about 5 mA/cm^2 for 20 min. The average porosity (P), i.e. the void fraction in the porous layer was evaluated by gravimetric method using the equation:

$$P = (m_1 - m_2)/(m_1 - m_3) \times 100\% \qquad (1)$$

Here m_1 is sample mass before the etching, m_2 after etching and m_3 after the removal of porous layer completely by rapid dissolution of the porous layer in 3% KOH solution. The thickness of porous silicon (d) was measured from:

$$d = (m_1 - m_3)/\rho S \qquad (2)$$

Where ρ is the silicon density (2.33 g/cm^3) and S is the etched surface.

Thin film of the pure tin (Sn) of about 100 nm was deposited onto silicon, porous silicon and glass substrates by evaporation in vacuum (5x10^{-5} bar). The thickness of the film was measured using a deposition controller (Inficon, Leybold). Conversion of Sn to n-type SnO was performed by oxidation in air at 300°C for 10 h.

The efficiency of the humidity response was defined as the ratio of the resistance difference under air (R_a) and humidity (R_h) to that in the air (R_a):

$$S_R = (R_a - R_h)/R_a (\times 100\%) \qquad (3)$$

Current-voltage characteristic*s* of n-SnO/p-PS/p-Si heterojunctions were measured in air and humid environment in special chamber. Resistances of SnO/p-PS/p-Si heterojunction were calculated from direct I-V-characteristics at fixed value of V= 2 V. The relative humidity (RH) was changed by evaporating of water inside of the chamber from 62% to 95% RH and measured by using "Extech-444701'' Hydron Thermometer. The capacitance values were measured using the IET 1920 Precision LCR meter at 1 MHz frequency.

X-Ray diffraction (XRD) analyses of the films were carried out using Bruker D2 Phaser (Germany) diffractometer in θ-2θ (10-70°) scan mode with Ni-filtered CuK$_\alpha$ radiation (λ=1.54060 A) source. Photoluminescence (PL) measurements were performed using PL/PLE/Raman spectrometer (Tokyo Instruments, Inc.). The emission of the samples were excited by 325 nm wavelength laser beams. The spectrometric ellipsometry measurements in 190–1700 nm spectral range were performed using Woollam M2000 rotating compensator instrument. Incident light angles were varied between 55° and 65° with 5° step. The Complete Ease computer program was used for the ellipsometric data fitting procedure.

All of the measurements were performed at room temperature.

3. RESULTS AND DISCUSSION

Typical XRD pattern of obtained SnO layer formed on glass is shown in Fig. 1. The XRD patterns reveal narrow peaks, characteristic for tetragonal lattice with a=3.8020 A and c=4.8360 A (Space group: P4/nmm) of the obtained films in agreement with the JCPDS card N° 01085 0423. The average grain sizes of SnO calculated using the Scherer formula from full-width half-maximum (FWHM) were found to be 64 nm. The density of SnO film is 6.399 g/cm^3.
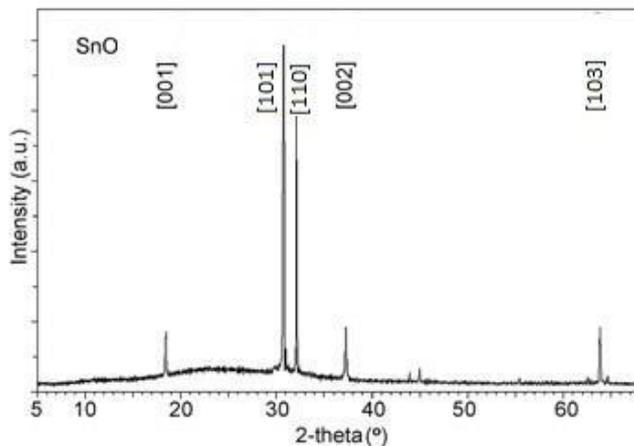
Fig.1. XRD patterns of the SnO film on glass substrate.
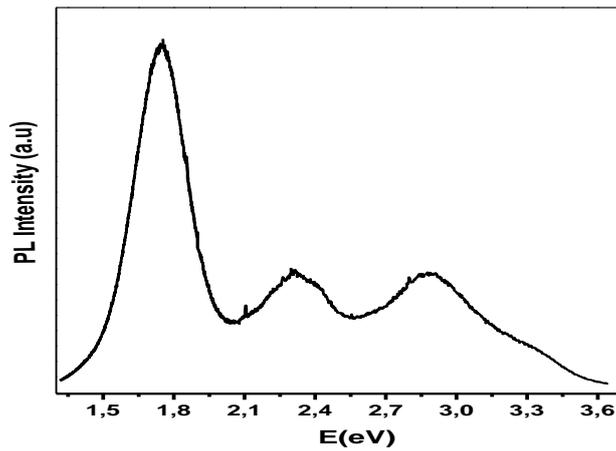
Fig. 2. Photoluminescence spectrum of SnO film on glass substrate.
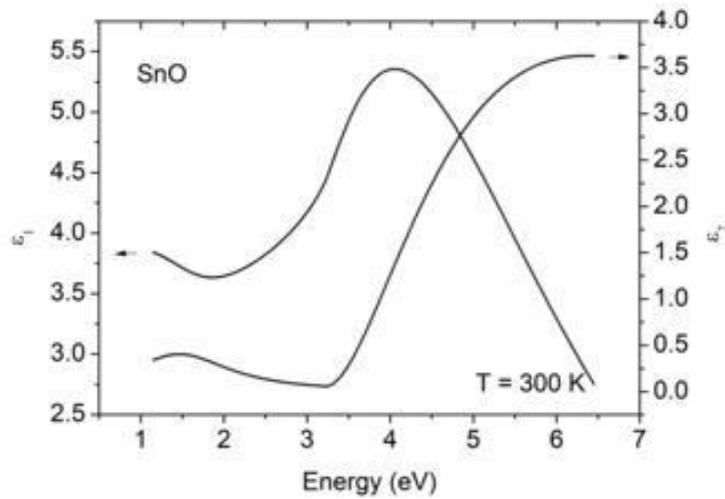
Fig. 3. Real (ε_1) and imaginary (ε_2) parts of dielectric function of SnO film on glass substrate.
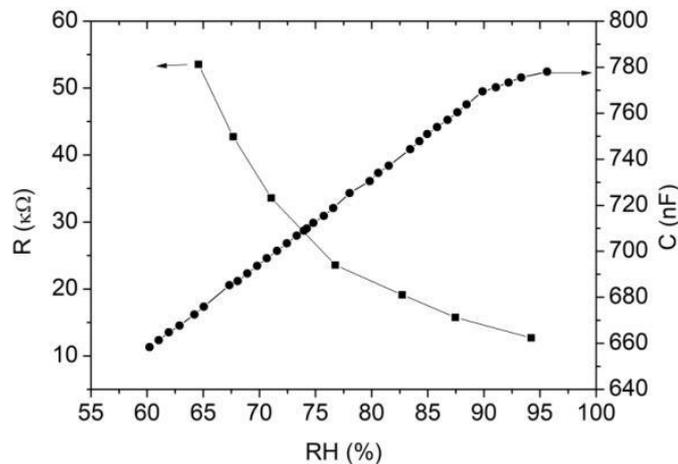
Fig.4. The dependence of resistance and capacitance of SnO/PS/Si heterostructure on relative humidity.

The photoluminescence spectrum of SnO film on glass substrate is displayed in Figure 2. The spectrum consist in a few wide bands at 1.75 eV, 2.3 eV, 2.9 eV and a shoulder at about 3.3 eV. The band around 3.3 eV can be evidently attributed to intrinsic optical transition in SnO film. This assumption is supported by spectroscopic ellipsometry measurements shown in

Fig.3. The transition at about 3.3 eV (see, imaginary part ε_2 of the dielectric function) is obviously due to the absorption at the fundamental band gap of SnO, which is also in good agreement with the optical absorption results, obtained in [17]. As for low-energetic bands in the PL spectrum, they generally can be related to crystal defects or defect levels associated with oxygen

vacancies, or tin interstitials that have formed during growth process [17].

Fig.4 illustrates the humidity dependence of resistance for SnO/PS/Si heterostructures. It is seen that resistance decreases from 55 kΩ to 10 kΩ with increase of the relative humidity from 65 to 95% RH. The humidity sensitivity of resistance of SnO/PS/Si heterostructure sensor at room temperature is about of 80%. The essential dependence on relative humidity

shows also heterostructure capacitance which increases from 650 nF to 780 nF [Fig.4].

It should be noted that for n-SnO/p-Si (without PS film) and p-PS/p-Si structures the noticeably change in I-V characteristics under humidity was not observed.

Fig.5 shows the response-recovery behavior of direct current at V=2V of the SnO/PS/Si sensor after successive cycles of placing in a humid environment. It can be seen that the response time is about 1 min.
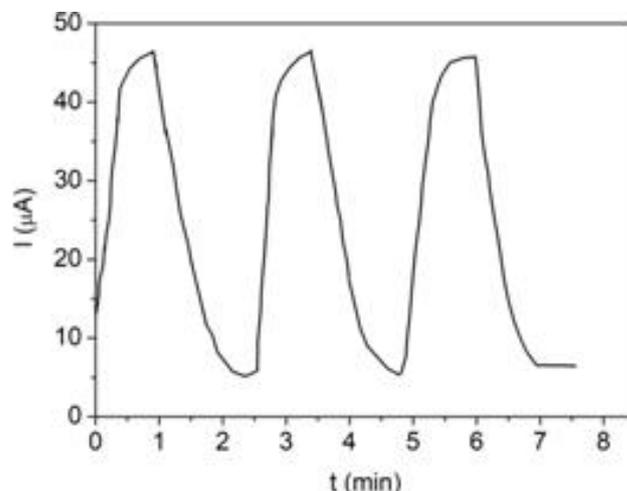
Fig.5. The current response of SnO/PS/Si sensor as a function of storage time on the successive placing in air (65%RH) and humid environment (95%RH).

To summarize, the following experimental facts related to change of the electrical characteristics after placing the SnO/PS/Si heterostrutures in humid atmosphere (300 K) were solidly established:

1) XRD analyses of the nanoparticle thin films SnO n-type (about 100 nm) prepared by oxidation the pure tin to SnO film in air at 300ºC, show tetragonal lattice with a=3.8020 Å, b=4.8360 Å and the average grain sizes of SnO about 64 nm.

2) The photoluminescence and optical measurements show that forbidden band around 3.3 eV can be attributed to intrinsic optical transition in SnO film.

3) Placing SnO/PS/Si structures in humid environment results in both the forward and reverse current of I-V characteristics.

4) For SnO/PS/Si structures the forward conductivity increases (resistance decreases from 60 kΩ to 10 kΩ) with rise of the relative humidity (from 65 to 95% RH).

5) This phenomenon is reversible, for SnO/PS/Si structures, inserting and removing the structure from H_2O is the response and recovery of the conductivity.

6) However, when the SnO/Si structures (without PS film) were placed in a humid environment, noticeable electricity change was not observed.

The gas-stimulated function mechanisms for resistance or capacitance type porous silicon-based sensors are generally associated with a change in the carrier concentration in porous layer due to the

absorbed molecules or change in dielectric constant as a result of gas concentration inside the pores.

In contrast to gas-stimulated mechanism, the mechanism involved in the sensing response of SnO/PS/Si heterostructure to humidity is rather complicated. The sensing mechanism consists in the dissociation of H_2O molecules at the surface of the SnO nanostructure [12]. One of the two O-H bonds cleaves resulting in one OH^- that bond to Sn^{4+} sites, meanwhile H^+ bonds to an oxygen atom from the SnO lattice. The H^+ ions, which diffuse into n-SnO and meet with free electrons, become neutral. Both hydrogen and OH^- particles passing cross of the n-SnO/p-PS contact reach the nanostructure region of p-PS [8]. Further, the concertation of holes increases because of interaction of H_2 and OH^- with nano-defects of the p-type porous silicon (Si-O and Si-H grains). In fact, thickness of the hole accumulation layer increases (the resistance decreases) in nanostructure porous silicon and therefore the resistance decreases with increase of humidity in SnO/PS/Si heterojunction.

4. CONCLUSIONS

SnO thin films are fabricated on porous silicon, silicon, glass substrates by means of conversion of pure Sn into SnO by oxidation in air at 300ºC for 10 h. The structural, optical and electrical properties of thin films SnO and SnO/PS/Si heterostructures are studied. Thin films reveal a tetragonal symmetry (Space group: P4/nmm) with lattice parameters a=3.8020Å and c=4.8360Å and average grain size of 64 nm. The current-voltage characteristics of SnO/PS/Si

heterostructures are measured at humidity and at room conditions. Humidity-resistance and humidity-capacitance effect of SnO/PS/Si heterostructures are observed with the sensor response to H_2O molecules about of 30% (at relative humidity 65-95%). The mechanism for humidity-stimulated electricity in SnO/PS/Si heterostructures is discussed.

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