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Study of porous silicon humidity sensor vapors by photoluminescence quenching for organic solvents

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ABSTRACT

In this paper a humidity sensor based on Photoluminescence (PL) response of porous silicon (PS) to specific amounts of organic vapors of ethanol, *n*-hexane and trichloroethylene in gas phase. PL quenching measurements in a controlled humidity atmosphere mixed Nitrogen gas and water vapor were performed to test the sensor response towards the water vapor. Surface morphologies of the PS samples were characterized by an atomic force microscopy (AFM), structural properties were investigated via X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy, reflectivity for bulk and PS is investigated. The PL for the sample is determined in air and different organic vapor chemical like Ethanol, *n*-Hexane and Trichloroethylene.

The PL spectrums of PS we find improve of PL intensity, and PL quenching of PS in presence of organic species by decrease radiative recombination of excition with increasing effective dielectric constant the coulombic force between electron and holes as well as their recombination are lowered.

1. Introduction

With the recent development in nanotechnology there is a pressing need for stable chemical vapor sensors with a high efficiency, quickly sensing and low power consumption [1]. Trichloroethyelene, Ethanol and *n*-Hexane are organic vapor used as industrial solvent for cleaning product and personal care product, sensing organic vapor is important because it is among the most hurtful gases and possibly poisonous to the human [2]. The development lead to obtain sensor is inexpensive and enable multiplexing of sensor arrays and remote sensing [3,4]. Vapor sensor use various detection principles like electrochemical and catalytic or optical detection [5].

PS is promising material and has attracted much attention in the field of sensor technology because it's diverse application for detection of different analyte [6]. Application PS as sensor involve different type of sensor such as optical sensor the principle of the optical sensing based porous silicon layer is variation in optical properties due to interaction between PS layer and vapors of solvent solution we can consider PS is convenient and inexpensive optical devices for detection organic solvent [7,8]. PS has a unique property make it attractive for these application include increased surface interaction area, simplicity and repeat ability of fabrication and compatibility with well-established [9]. The sensing mechanism is based on a

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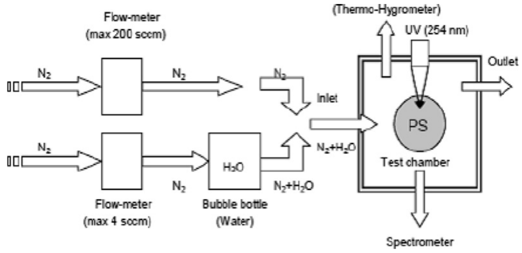

Fig. 1. Experimental set-up to sense water vapor.

change in physical properties of PS when it is exposed to analytes.ps based vapor sensor must they have to respond quickly, accurately and sensitivity [10].

The first use PS in sensor application were based on variation of its electrical properties such as capacities and conductivity [11,12]. They both depend very much on the porosity of the layer of PS. the size and distributions of pores of PS sensor play crucial role in determine the sensitivity and response time [13]. The porosity and pore morphology of PS depend on parameter like concentration of electrolyte, etching time, etching current density and bulk doping of the silicon wafer [14].

Now optical properties of PS have been exploited for vapor sensing because their fast response time. The most optical technique are depend on change in optical reflectivity and photoluminescence [15,16], The properties of PS such as PL that is observed by Canham in 1990 [17]. We can define this phenomena is when the sample is absorption photon and then emission it, the basic principle of PL technology is the ability of the material to absorb and store light energy and emit the stored energy as visible light [18].

The emission of light from PS is take place in the visible region of the electromagnetic spectrum. The wavelength of the emitted light from PS is dependent on the porosity such as the sample is highly porous emit Green/Blue light, whereas the sample less porous emit red light [19]. PL can provide information on the quality and purity of the material, PL is take different form resonant radiation, fluorescence and phosphorescence [20].

In this short paper using PS sensor for determination organic vapor Trichloroethylene, Ethanol and *n*-Hexane at room temperature with low concentration the detectable organic based on the PL observed from PS is quenched when exposure to organic solvent the effect of organic on PL is discuss upon dielectric constant of the organic, there are application associated with environmental many industries.

2. Experimental details

PS layer was produced by anodization etching of (100) oriented p-type Si wafers with resistivity 1.5–5 Ω cm and (550 ± 50) μm thickness. We doped the back faces of Si wafers with boron, before starting etching process we divided Si wafers into small pieces in dimension nearly of 2 × 2 cm these samples were etched in the electrolyte consisted of Hydrofluoric acid (HF 48%) and Ethanol (C_2H_5OH 99.9%) HF concentration in the solution is 20% in a current density 15 mA/cm^2 for 15 min time etching. The role of ethanol in the electrolyte to reduce surface tension and improving the homogeneity and uniformity of the PS layer by promoting hydrogen bubble removal. To achieve anodization etching we use the Teflon cell resistant to HF, the Si sample act as anode, while the cathode was gold conducting material and resistant to HF. After anodization sample was rinsed in ethanol and pentan and dried in the ambient. The surface profile of PS was analyzed by AFM (CSPM-AA3000). The FTIR transmission spectrum on the PS layer was recorded by (SHIMADZU) spectrometer in the range of 400–4000 cm^{-1}. Reflectivity Obtained by using (TF-Probe SR300 USA) for bulk and PS is investigated. The PL for the sample is determined in air, nitrogen and different organic vapor chemical like Ethanol, *n*-Hexane and Trichloroethylene. The PS sample was then placed in a chamber containing a mixture of nitrogen and with various chemical solvents vapor to measure its luminescence response to solvent vapor. Etching process and all sensor measurements were carried out at room temperature.

The PL quenching measurements of PS were performed in sensor test chamber which is made from Teflon for sensing of water vapor. Schematic diagram for the sensor test chamber and other required equipment are shown in Fig. 1 where, nitrogen gas was used as a carrier gas for water vapor. Two flow-meters bought from Sierra Instruments (smart track 100 and micro track 101) which have maximum flow 200 sccm and 4 sccm were used as a nitrogen gas controller. Nitrogen gas was separated into two lines. A line was connected to a bubble bottle to obtain water-gas mixture.

3. Results and discussion

The morphology of PS sample examined by AFM. Fig. 2 shows three dimension of PS layer. From this images can observe the PS has sponge like structure with densely pores in which the irregular and randomly distributed nanocrystalline silicon pillars and voids over the entire surface can be seen.

Fig. 3 shows XRD pattern of bulk silicon and PS. A distinct different between bulk Si and PS can observed the peak become broad with varying (FWHM) for PS sample, the mismatch between Si and PS because in PS the ray diffraction from crystals with nanosize in the walls between pores. Consequently, we can confirm that the PS layer remains crystalline, but it is

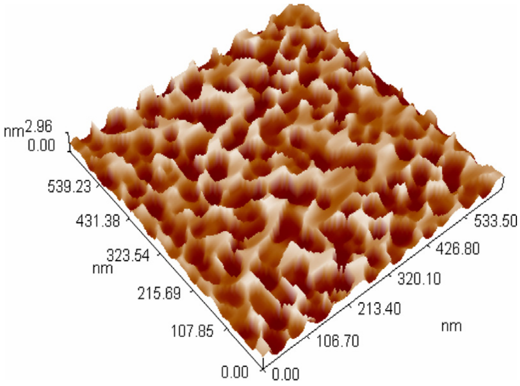

Fig. 2. 3D AFM images of PS sample of PS layer prepared at 15 mA/cm^2, etching time 15 min and HF_c = 20%.

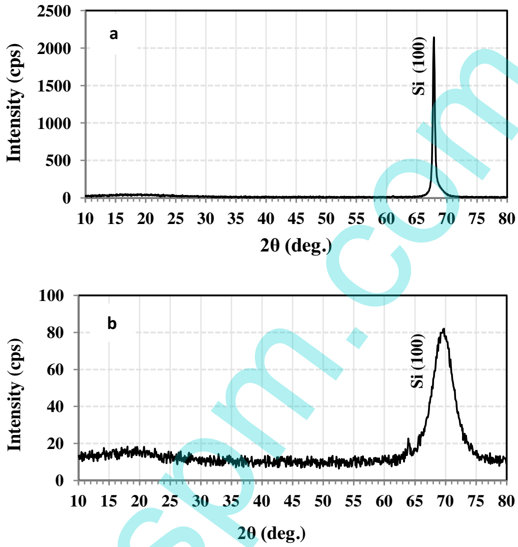

Fig. 3. XRD pattern of (a) c-Si and (b) PS layer prepared at 15 mA/cm^2, etching time 15 min and HF_c = 20%.

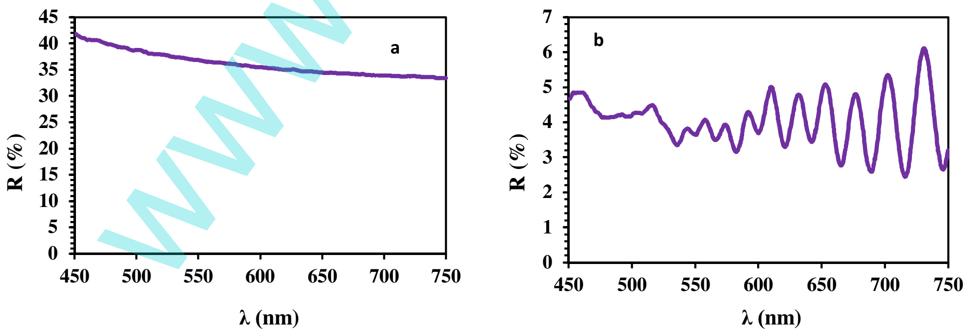

Fig. 4. Reflectivity of (a) c-Si and (b) PS layer prepared at 15 mA/cm^2, etching time 15 min and HF_c = 20%.

slightly shifted to a smaller diffraction angle. This result is attributed to effect of strain which leads to a little expanded lattice parameter and then PS peak is displaced to small diffraction angle diffraction and when crystalline size of PS decreasing.

Fig. 4a presents the reflectivity of bulk silicon as a function of wavelength the reflectivity has a maximum value about 42% at wavelength 450 nm and its value decrease with increasing wavelength and minimum value reflectivity 33% at wavelength 750 nm this relatively high reflectivity of silicon in 450–850 nm is due to the large refractive index discontinuity exists at air–silicon interface.

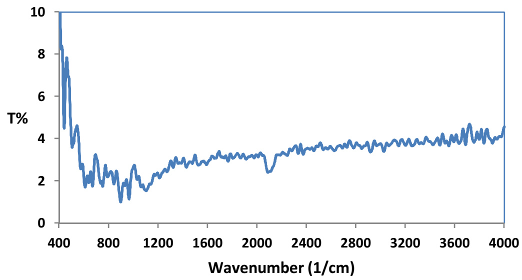

Fig. 5. A plot of transmittance vs. wavenumber for PS prepared at 15 mA/cm^2, etching time 15 min and $HF_c = 20\%$.

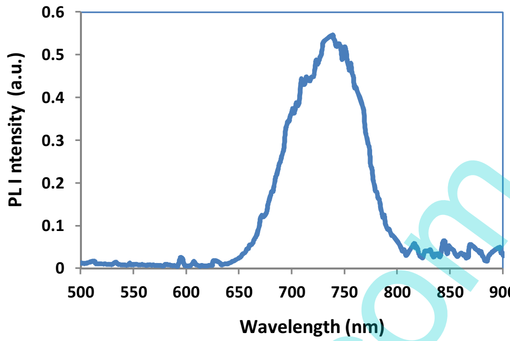

Fig. 6. A plot of PL spectrum for PS layer prepared at 15 mA/cm^2, etching time 15 min and $HF_c = 20\%$.

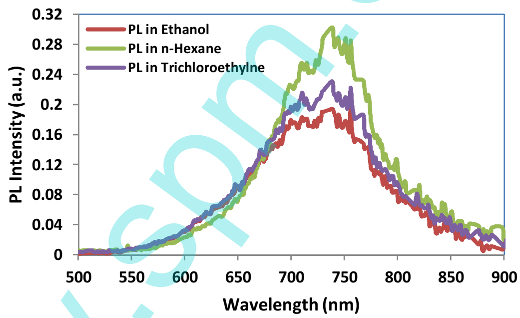

Fig. 7. A plot of PL spectra of PS layer prepared at 15 mA/cm^2, etching time 15 min and $HF_c = 20\%$ for different vapors organic chemical solvents.

Fig. 4b PS shows low reflectance due to their texture surface, the incident photon can be trapped effectively on the surface of PS. A porous layer on top of the Si wafer may play an efficient role in diminishing the amount of reflected light from the Si wafer, the reflectance is a function of wavelength. when incident light strikes PS, light can reflected both off the top and also the bottom of the porous layer allowing the reflected light to interfere and produce interference fringes [21] is one of the most important property of PS is refractive index this property controls the reflection and transmission of wave incident on the PS–air interface, the refractive index is depend on porosity where is decrease with increasing porosity because the pore is mixture of air and silicon.

Surface chemical composition of PS is best probed with FTIR. The FTIR spectra of the PS are shown in Fig. 5, the large specific area of PS and chemical properties of the surface has an effect on the electrical, optical and mechanical properties. The pore surface includes a high density of dangling bond of Si for original impurities such as hydrogen and fluorine [22]. The impurities come from the electrolyte used for electrochemical etching and from the ambient air. The transmittance peak at 611.43 cm^{-1} Si–Si stretching in 669.3 cm^{-1} Si—H wagging mode, 842.89 cm^{-1} Si—O bend in O—Si—O.

The PL spectrum of PS at room temperature is shown in Fig. 6 an expected broad band emission was measured with the pronounced peak around 670, 700, 730, 760 nm the PL emission is attributed to quantum confinement, also the emission from defect state in surface oxide might contributed to the luminescence [23,24].

From Fig. 7 shows effect of the organic vapors chemical Ethanol, *n*-Hexane and Trichloroethylene solvents on PL spectra that same chemical nature and different physical parameter due to increasing length of carbon chain. For all organic vapors the PL intensity is reduction from than in air (PL quenching) the quenching of PL intensity extent approximately with the dipole moment of organic vapors [21]. The molecule with large dipole moment like Ethanol and *n*-Hexane quench PL of PS to large (>80% loss PL intensity) this phenomenon interpreted as the stabilization of surface trap by alignment of molecular dipoles on the PS surface. Where nonradiative emission processes dominate the recombination rate [25] due to attraction of electron and holes of surface trap [26]. When use trichloroethylene the PL quenching is less than other vapors chemical because the dipole moment is less the value of dipole moment for the organic solvents because the larger dipole moment in Ethanol that lead to PS surface nonradiative emission processes dominated the recombination rate, and presence of organic species by decrease radiative recombination of excition with increasing effective dielectric constant (Ethanol 24.5, Trichloroethylene 3.39, *n*-Hexane 1.88) the coulombic force between electron and holes as well as their recombination are lowered.

4. Conclusion

Sample of PS were prepared by anodized etching. AFM confirmed the nanocrystaline of the sample; XRD indicated the PS nanocrystalline structure. the morphological properties is effected on optical properties PS such as reflectivity's where it decrease when the porous layer is obtained on Si wafer, the PL emission from nanostructure is attributed to the nanoscale size of the Si due to quantum confinement effect of the PS the PL Is function of the level concentration of different organic vapor chemical and PL is sensitive to type of organic vapor chemical solvents.

The PL spectrums of PS we find improve of PL intensity, and PL quenching of PS in presence of organic species by decrease radiative recombination of excition with increasing effective dielectric constant the coulombic force between electron and holes as well as their recombination are lowered.

It is possible to conclude that PS surface is a promising candidate material to be used as a humidity sensor.

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