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Polymer functionalized nanostructured porous silicon for selective water vapor sensing at room temperature

Priyanka Dwivedi, Samaresh Das, Saakshi Dhanekar*

Centre for Applied Research in Electronics (CARE), Indian Institute of Technology (IIT), Hauz Khas, New Delhi 110016, India

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This paper highlights the surface treatment of porous silicon (PSi) for enhancing the sensitivity of water vapors at room temperature. A simple and low cost technique was used for fabrication and functionalization of PSi. Spin coated polyvinyl alcohol (PVA) was used for functionalizing PSi surface. Morphological and structural studies were conducted to analyze samples using SEM and XRD/Raman spectroscopy respectively. Contact angle measurements were performed for assessing the wettability of the surfaces. PSi and functionalized PSi samples were tested as sensors in presence of different analytes like ethanol, acetone, isopropyl alcohol (IPA) and water vapors in the range of 50–500 ppm. Electrical measurements were taken from parallel aluminium electrodes fabricated on the functionalized surface, using metal mask and thermal evaporation. Functionalized PSi sensors in comparison to non-functionalized sensors depicted selective and enhanced response to water vapor at room temperature. The results portray an efficient and selective water vapor detection at room temperature.

1. Introduction

Water vapor sensing is being studied and tested for the past three to four decades now. The water vapor measurement is done in growing plants, electrical devices, food industry, wireless sensors and environmental monitoring [1–4]. The importance of water vapor measurement led to the development of sensors with higher sensitivity, response time and longer stability. The different types of humidity sensors are based on water phase protonic ceramic materials, polyvinyl alcohol dielectric films, polymers, multi wall carbon nano tubes, pristine carbon nano tubes, resistive and capacitive configuration [5–8]. All these different materials are used in the development of sensors because of their hydrophobic/hydrophilic property. Functionalization plays a key role in improving selectivity, surface properties and stability of surface. Room temperature sensing remains a challenge as most of the sensors operate at higher temperatures [9,10]. There is a great emphasis on preparation of nano-sensors which can function at room temperature. Nano-porous silicon is a network of nano crystallites with large number of nano pores and known for its tunable morphology, enhanced sensitivity and large surface area-to-volume ratio [11–13]. Functionalization of such a surface can make it selective for a particular gas/vapor and also improve its performance.

In the present work, the fuctionalization is done by poly vinyl alcohol (PVA), which is a water-soluble polymer was spin coated on PSi for two cycles at constant rpm. PSi and functionalized PSi samples have been analyzed using field-emission

* Corresponding author.
E-mail address: sdhanekar@care.iitd.ac.in (S. Dhanekar).

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scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), Raman Spectroscopy, Photoluminence, and contact angle measurements. Sensors based on both PSi and its counterpart were tested in real time in presence of different analytes in the range of 50–500 ppm.

2. Experimental work

2.1. Fabrication process

Sensor fabrication process was done using p-type silicon (Si) wafer with resistivity 1–10 Ω-cm. Wafer cleaning was performed using degreasing followed by piranha cleaning. Since, native oxide gets formed on the surface after piranha cleaning therefore before PSi fabrication, the wafers were dipped in buffered hydrofluoric acid (BHF). PSi fabrication was done using electrochemical etching using electrolyte solution of HF and ethanol in 1:1 ratio. There are few important parameters which effect the morphology of PSi like electrolyte solution, current density and etching time. Several samples were prepared and the ones with smallest pore size were used for sensor fabrication, which were prepared at current density 100 mA/cm^2 for 3 min. Process starts with thermal evaporation used for depositing aluminium on the back side of silicon (Fig. 1(a)) for PSi fabrication (Fig. 1(b)). This was followed by spin coating of PVA which was prepared using 1.5 g PVA solution in 50 ml of deionized water (Fig. 1(c)). Two cycles of spin coating at 4000 rpm was performed for removal of large aggregates. Spin coated sample was baked at 60 °C for 2 min using hot plate. Parallel electrodes were formed for taking electrical connection using metal mask and evaporating aluminium using thermal evaporation (Fig. 1(d)).

2.2. Characterization and sensor testing

The morphologies of all samples were analyzed by FEI Quanta 200 F SEM. Thickness was checked using stylus surface profiler (KLA Tencor, Alpha step IQ). Raman spectroscopy for structural analysis was done using LAbRAMHR Evolution RAMAN Spectrometer (Horiba) with Ar laser excitation wavelength 514 nm. The crystal structure was studied by XRD (Phillips X'Pert, PRO-PW 3040 diffractometer) with glancing angle 0.5°. Surface wetting properties were verified by contact angle measurements using sessile drop technique.

Sensing studies were carried out using sensing setup described elsewhere as follows [13]. The sensor was placed in the test chamber. The flow of nitrogen gas used as a carrier gas, was controlled by mass flow controller (MFC). The analyte vapors were introduced into the test chamber by passing N_2 through the bubbler containing analyte at certain temperature to maintain vapor pressure. The concentration (ppm) of analytes inside the chamber was calculated using the ppm and vapor pressure relationship [14].

3. Result and discussion

3.1. Morphology analysis

The morphology information of any porous material can be obtained in detail by using SEM micrograph. Fig. 2(a) shows the SEM of as-anodized PSi. The homogeneous distribution of the pores on the surface of the samples is clearly visible with an

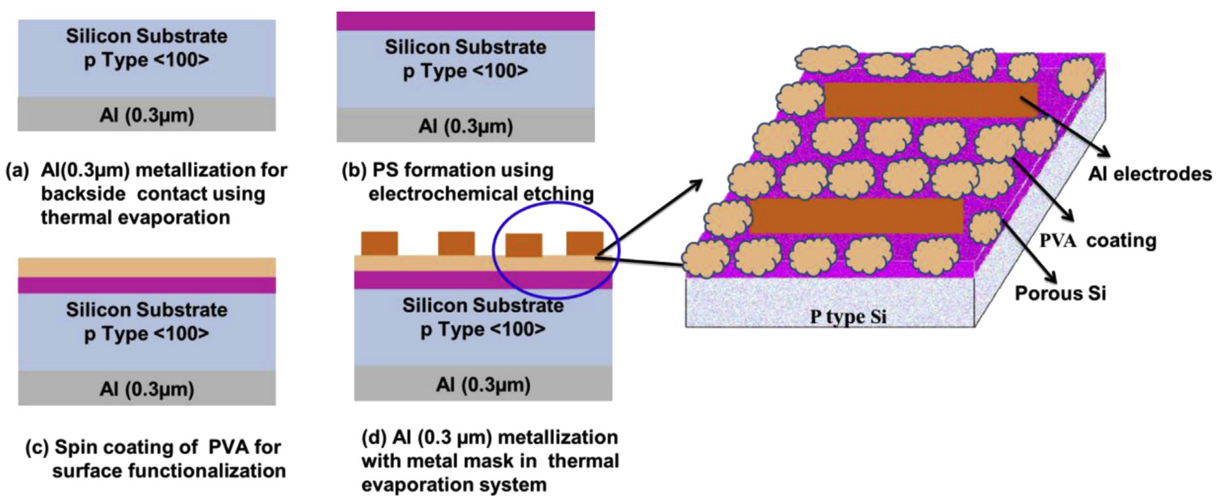

Fig. 1. Process flow for sensor device fabrication.