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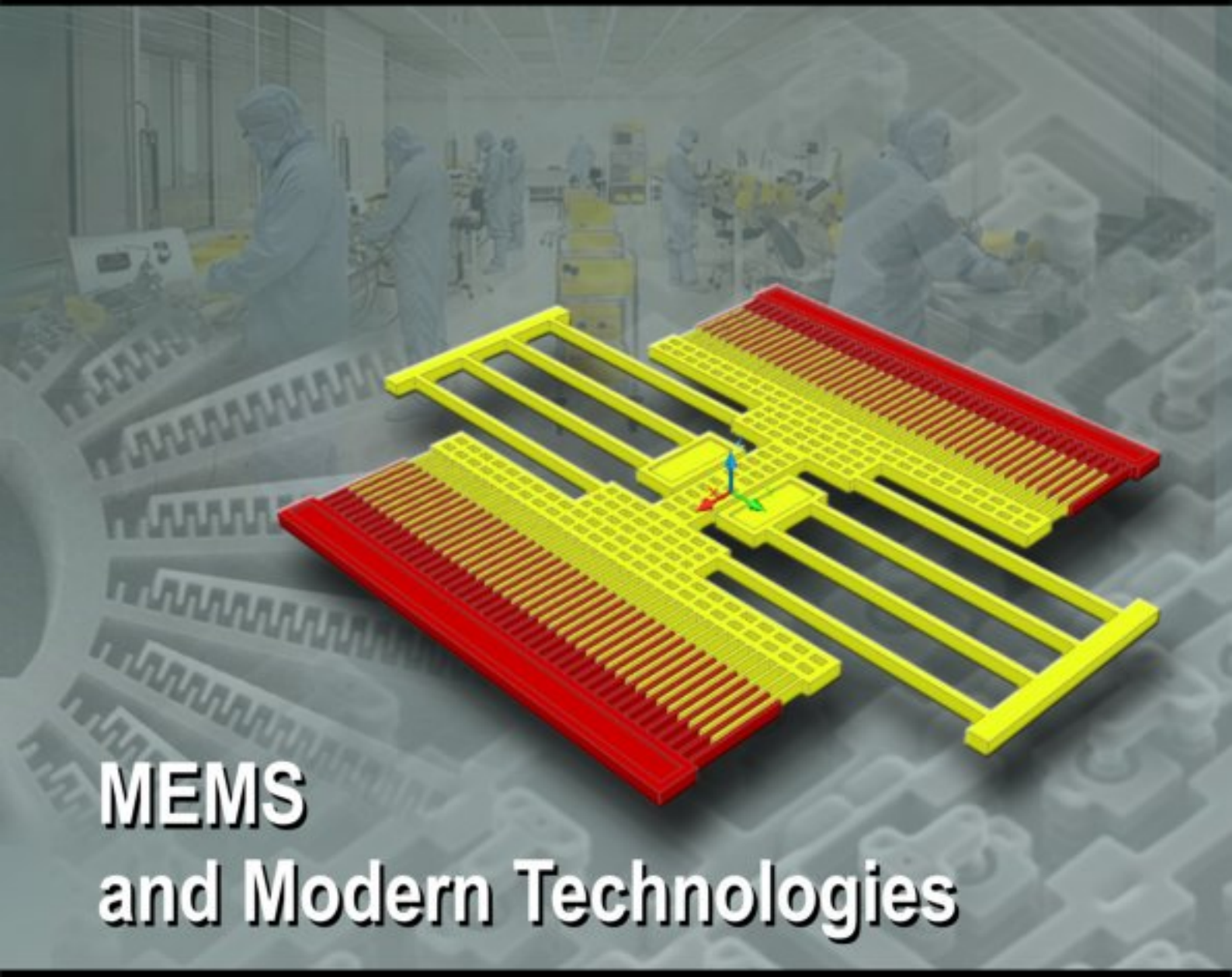

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Contents

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Porous Silicon Hydrogen Sensor at Room Temperature: The Effect of Surface Modification and Noble Metal Contacts

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Abstract: Porous silicon (PS) was fabricated by anodization of p-type crystalline silicon of resistivity 2-5 Ω cm. After formation, the PS surface was modified by the solution containing noble metal like Pd. Pd-Ag catalytic contact electrodes were deposited on porous silicon and on p-Silicon to fabricate Pd-Ag/PS/p-Si/Pd-Ag sensor structure to carry out the hydrogen sensing experiments. The Sensor was exposed to 1% hydrogen in nitrogen as carrier gas at room temperature (27^0C). Pd modified sensor showed minimum fluctuations and consistent performance with 86% response, response time and recovery time of 24 sec and 264 sec respectively. The stability experiments were studied for both unmodified and Pd modified sensor structures for a period of about 24 hours and the modified sensors showed excellent durability with no drift in response behavior. *Copyright © 2009 IFSA.*

Keywords: Porous silicon, Pd surface modification, Heterojunction, Hydrogen sensor, Stability

1. Introduction

Hydrogen is gaining interest as the promising source of cost effective and clean alternative fuel in near future. Hydrogen is also used in the production of industrial chemicals and food products. But safety is an important issue while using hydrogen - an odorless and colourless gas with an explosion limit 4.65% to 93.9% in air. Commercially available sensors can detect the presence of hydrogen but have limitations related to cost, speed of operation, susceptibility to interference from other gases and temperature range etc. Numerous approaches are being pursued to develop the hydrogen sensors, including silicon and oxide based thin film devices with an aim to overcome these problems [1-4].

Porous silicon (PS), obtained conventionally by anodisation of crystalline p-type silicon, is a potential platform for high efficiency gas sensors mainly due to its very large surface to volume ratio, which enhances adsorption of the sensing gas, a primary step for gas sensor [5-6]. Also the high chemical reactivity of PS with the environment and the possibility of porosity control by the variation of the formation parameters further create an interest in sensing applications. Additionally, it is easy to fabricate sensors using PS with compatibility to silicon IC technology. Despite all the above advantages, problems such as stability, reversibility, and selectivity requires investigation in details for its commercial use. Though some of these problems have been addressed before [7, 8], the stabilization of PS and minimization of electrical drift in the actual device performance are still two major barriers against the fabrication of PS based devices for field applications. Several treatments to stabilize the PS structure have been reported e.g. controlled thermal oxidation, nitridation, halogenation and polymerization etc. Surface passivation by noble metals may also be very useful, as reported in the literature [9, 10]. For gas sensor applications, the aim of Pd modification is two-fold. First of all, to passivate the surface by noble metals to get long term stability and then to improve the electrical response in presence of gases due to its catalytic effect, while maintaining the large specific surface area of PS.

Palladium doped PS based hydrogen sensor was first reported by Polishchuk and co-workers [11] using contact potential difference variations (CPD). K. Luongo el al [12] reported a room temperature impedance H_2 sensor using nano structured Pd doped layer on the nano porous silicon surface. P. K. Sekhar and co workers tried to find out the influence of anodisation current density and etching time during PS formation on the response time and stability of Pd doped sensors using the same electrode configuration as reported earlier. [13]. In 2006 Rahimi et al. worked on the important parameters for Pd growth on PS by electroless plating and briefly observed the response to hydrogen for both lateral and sandwich structures using comb like gold electrical contacts [14].

In this paper, we specifically focus on the fabrication of a stabilized porous silicon based hydrogen sensor after modifying the PS surface using noble metal ion like Pd by a simple, reliable and a low cost chemical method. The response behavior, time of response and recovery, reproducibility and long term stability are reported here.

2. Experimental

The nanocrystalline PS samples were prepared by the electrochemical etching of p-type Si wafers of (100) orientation and 2-5 Ω cm resistivity using a mixture of HF and ethanol (7:3) as electrolyte. The porosity and thickness of the PS layers (55% and 5 μm) were measured gravimetrically using a precision semi microbalance type, 290-9842/K of PAG OERLIKONAG CH-DIETKON (Switzerland) [15]. After formation, PS samples were dipped into 10% HF solution for 10 sec to remove the native oxide layer and were immediately dipped into the weak acidic solutions (0.01 M) of $PdCl_2$ for 5 sec. Subsequently the samples were rinsed gently by DI water and dried in air followed by annealing in air at 110^0C for 10 min inside an electric oven. Different set of experiments was carried out to optimize modification time and solution strength. Pd-Ag (26%) catalytic metal electrodes (Ag was alloyed to Pd to prevent deterioration of Pd surface due to hydride formation) of the dimension 2 mm x 2 mm and thickness 0.2μm were deposited on the unmodified and modified porous silicon surfaces and on the bottom p-Si surfaces of the samples by e-beam evaporation using an Al metal mask. Thin copper wires were connected to these metal electrodes using silver paste for electrical measurements. The sensor structure was effectively a back-to-back Schottky configuration.

For the sensor study the samples were placed inside a closed corning glass tube with inlet and outlet provisions for gases. The tube was placed coaxially inside a resistively heated furnace with a 4 cm constant temperature zone. High purity hydrogen and nitrogen were used for the experiments. To

measure and to control the flow rates of the gases precisely throughout the experiments, mass flow meters and controllers (Digiflow, USA) were used. The current-voltage characteristics were studied by the Keithley Pico ammeter-voltage source (model 6487).

3. Results

The schematic of the gas sensor device with Pd-Ag/PS/p-Si/Pd-Ag structure is given in Fig. 1. The sensors were studied with 1% hydrogen in nitrogen as carrier gas. The response is defined here as the change in current in presence of hydrogen to the current in air at constant voltage in the forward bias mode and is expressed as $S=\left(\frac{I_a - I_g}{I_a}\right)_V$ where I_a is the current in air and I_g is the current in presence of gas. The detail sensor studies were carried out at room temperature (27 ^{0}C) as the sensor gets damaged at higher temperatures mainly due to the surface of PS.

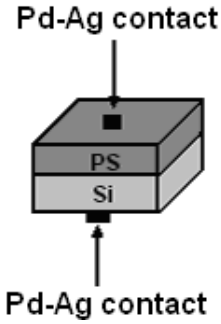

Fig. 1. Schematic of sensor geometry.

Fig. 2. shows the response-voltage characteristics of unmodified and modified PS sensors having Pd-Ag/PS/p-Si/Pd-Ag structures at room temperature in 1 % hydrogen gas mixed with nitrogen carrier gas. The maximum response for unmodified PS is 62 % at 0.9 V, whereas, in case of modified PS the maximum response obtained is 86 % at a lower bias of 0.5 V.

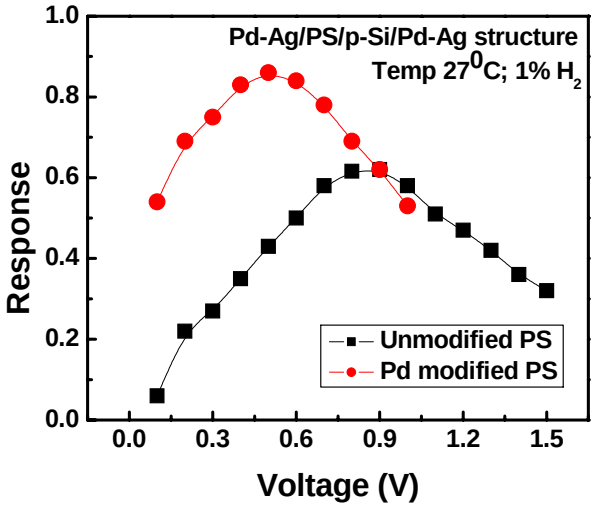

Fig. 2. Room temperature response-voltage characteristics of unmodified and Pd-modified PS sensors having Pd-Ag/PS/p-Si/Pd-Ag structures in 1 % hydrogen gas in nitrogen.

Fig. 3 shows the repeated cycle of unmodified and surface modified porous silicon hydrogen sensors operating at room temperature corresponding to their optimum biasing voltages. It is clear from the figure that the sensor response is more stable for Pd modified samples with a little drift in the base line value and with response and recovery time of 24 sec and 264 sec respectively. Table.1 presents the values of response, response time and recovery time of the unmodified and modified PS sensors. Fig. 4 demonstrates the transient response at different concentrations of hydrogen for unmodified and Pd modified PS sensors with Pd-Ag/PS/p-Si/Pd-Ag structure.

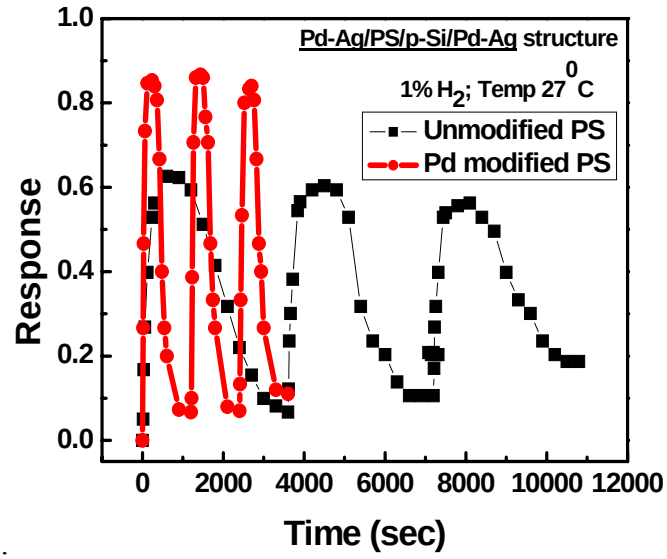

Fig. 3. Repeated cycle of transient response graph for unmodified and modified PS sensors having Pd-Ag/PS/p-Si/Pd-Ag structures.

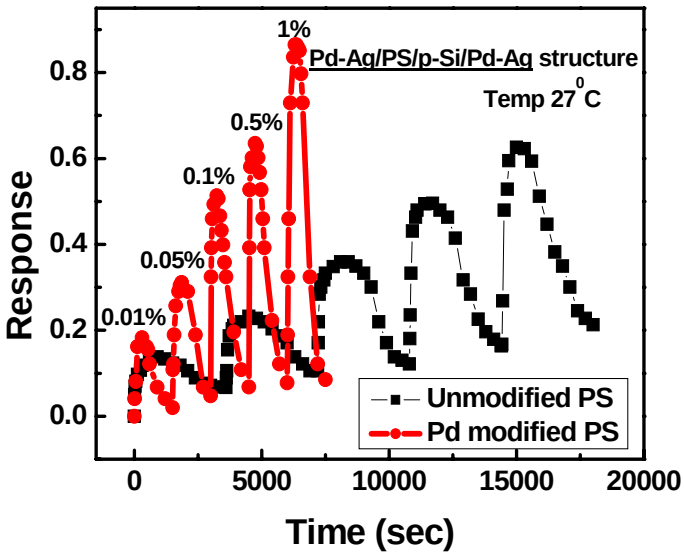

Fig. 4. Transient response at different concentrations of hydrogen for unmodified and Pd modified PS sensors with Pd-Ag/PS/p-Si/Pd-Ag structure.

Table 1. Sensing parameters for both unmodified and modified PS sensors having catalytic (Pd-Ag) contact electrodes.

Structure	Temperature (^{0}C)	Biasing Voltage (V)	Response (%)	Response Time (Sec)	Recovery Time (Sec)
Pd-Ag/PS/p-Si/Pd-Ag	27	0.9	62	131	1237
Pd-Ag/mod-PS/p-Si/Pd-Ag	27	0.5	86	24	264

The stability of both unmodified and modified PS sensors was tested with 1% hydrogen in nitrogen at 27 ^{0}C for 24 hours with duration of 8 hr per day at the biasing voltage corresponding to their optimum response and is shown in Fig. 5. It is clear from the figure that palladium-modified sensor shows the best consistency in stability.

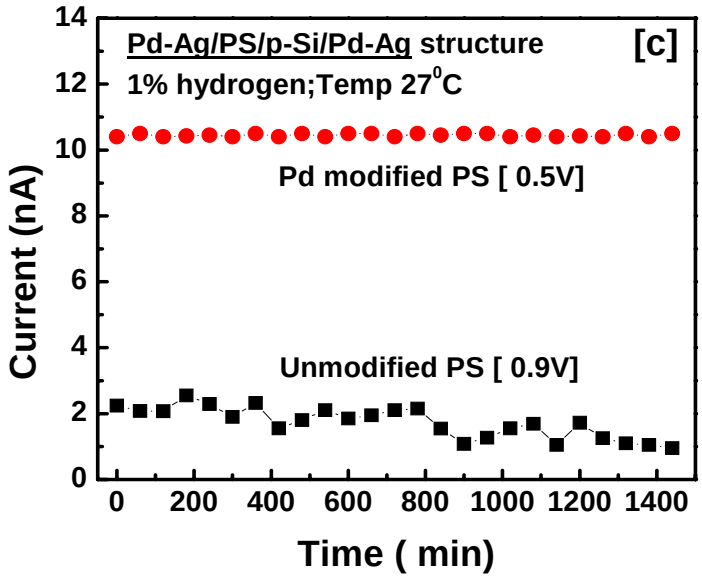

Fig. 5. Stability study for unmodified & Pd modified PS sensors with Pd-Ag/PS/p-Si/Pd-Ag structure.

4. Discussion

The Pd-Ag/PS/p-Si/Pd-Ag structure produces back-to-back Schottky barriers due to Pd-Ag/PS and Pd-Ag/p-Si junctions, with an additional PS/p-Si heterojunction. It is known that the porous silicon layer contains a large density of surface and interface states leading to Fermi-level pinning at the metal/PS interface. This may affect the electrical response of metal/PS junctions. Our results showed that the response and stability of a PS sensor improves much more when its surface is modified with noble metal. Dispersed noble metal islands over the PS surface react with some of the dangling electrons and passivate them. Oxygen molecules weekly bonded with the catalytic metal atoms dissociate yielding oxygen atoms. These oxygen atoms then undergo a spillover process and react with the remaining dangling electrons of PS surface and passivate the defect states to a large extent (which is also supported by our XPS results) and stabilize the material. During hydrogen sensing hydrogen molecule decomposes to hydrogen atoms on the catalytic metal surface and diffuse through the catalyst and reach the noble metal–porous silicon interface where a dipole layer forms [14, 16, 17] and reduces the work function of the metal. As a result the barrier height of the junction increases and the current decreases. Fig. 6a and 6b demonstrate the energy band diagram (not in scale) of the Pd-Ag/PS junction coupled to the dipole structure due to hydrogen diffusion, showing an increase in PS band bending in

presence of hydrogen and thus decrease in current. Our results further showed that Pd-Ag/p-Si interface does not contribute to the enhanced gas sensing but create a barrier against current flow. In reference to our earlier work [18] on Pd modified PS based Pd-Ag/PS/p-Si/Al sensor structure, where the response was comparable (84%) but the response time was much faster (~ 8 sec) we can infer that single Schottky junction is good enough for hydrogen sensing.

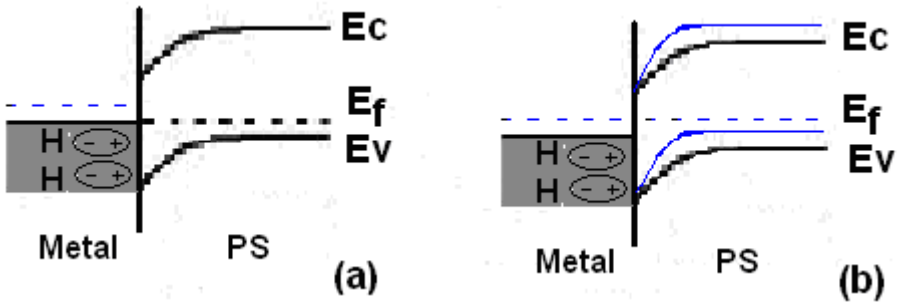

Fig. 6. Band diagram (not in scale) of Pd-Ag/PS junction coupled with a dipole layer during hydrogen sensing. (a) Decrease in metal work function due to the formation of a dipole layer at the interface by the diffused hydrogen (b) an increase in barrier height at the metal / PS junction.

5. Conclusion

Our experiments with Pd surface modified porous silicon on p-Si substrate in the form of back to back Schottky barrier junctions using Pd-Ag catalytic electrode contacts is useful as room temperature hydrogen sensor with appreciably high response and considerably fast response time. The stability of the modified sensor structure is visibly much improved compared to the unmodified one. The sensing mechanism is clarified in respect of hydrogen dipole structure and reduction in metal work function leading to an increase in barrier height of the junction in presence of hydrogen.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
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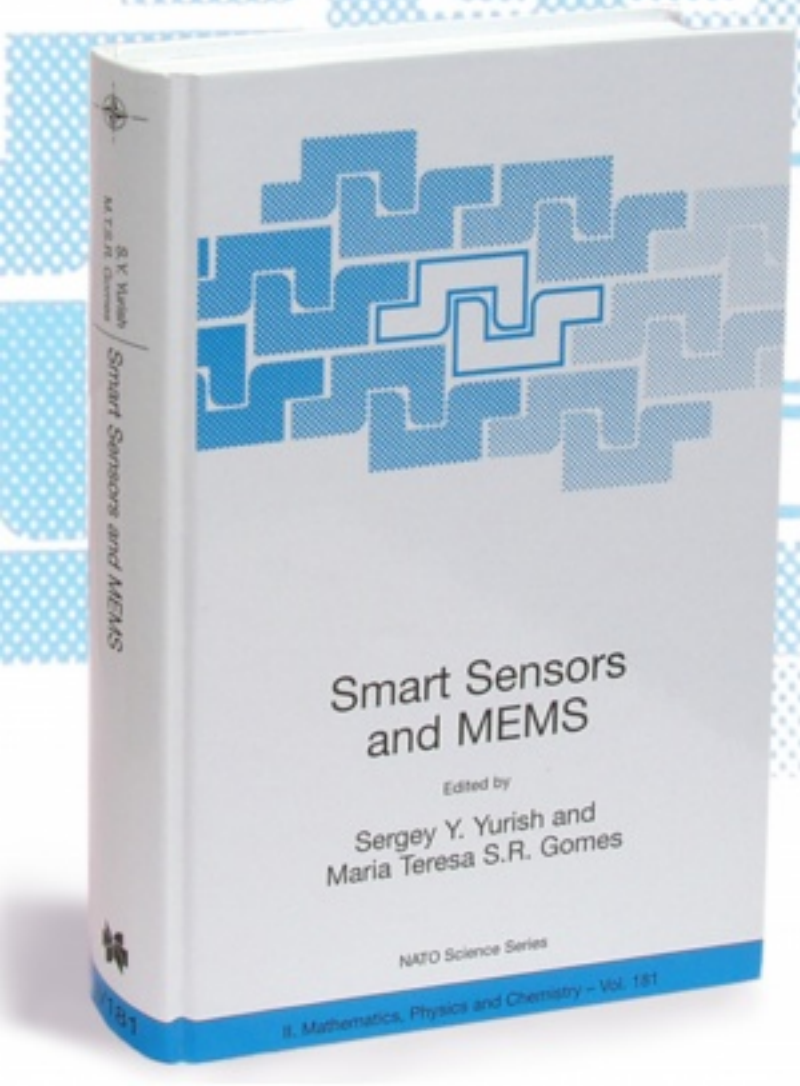

Smart Sensors and MEMS

Edited by

Sergey Y. Yurish and
Maria Teresa S.R. Gomes

The book provides an unique collection of contributions on latest achievements in sensors area and technologies that have made by eleven internationally recognized leading experts ...and gives an excellent opportunity to provide a systematic, in-depth treatment of the new and rapidly developing field of smart sensors and MEMS.

The volume is an excellent guide for practicing engineers, researchers and students interested in this crucial aspect of actual smart sensor design.

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