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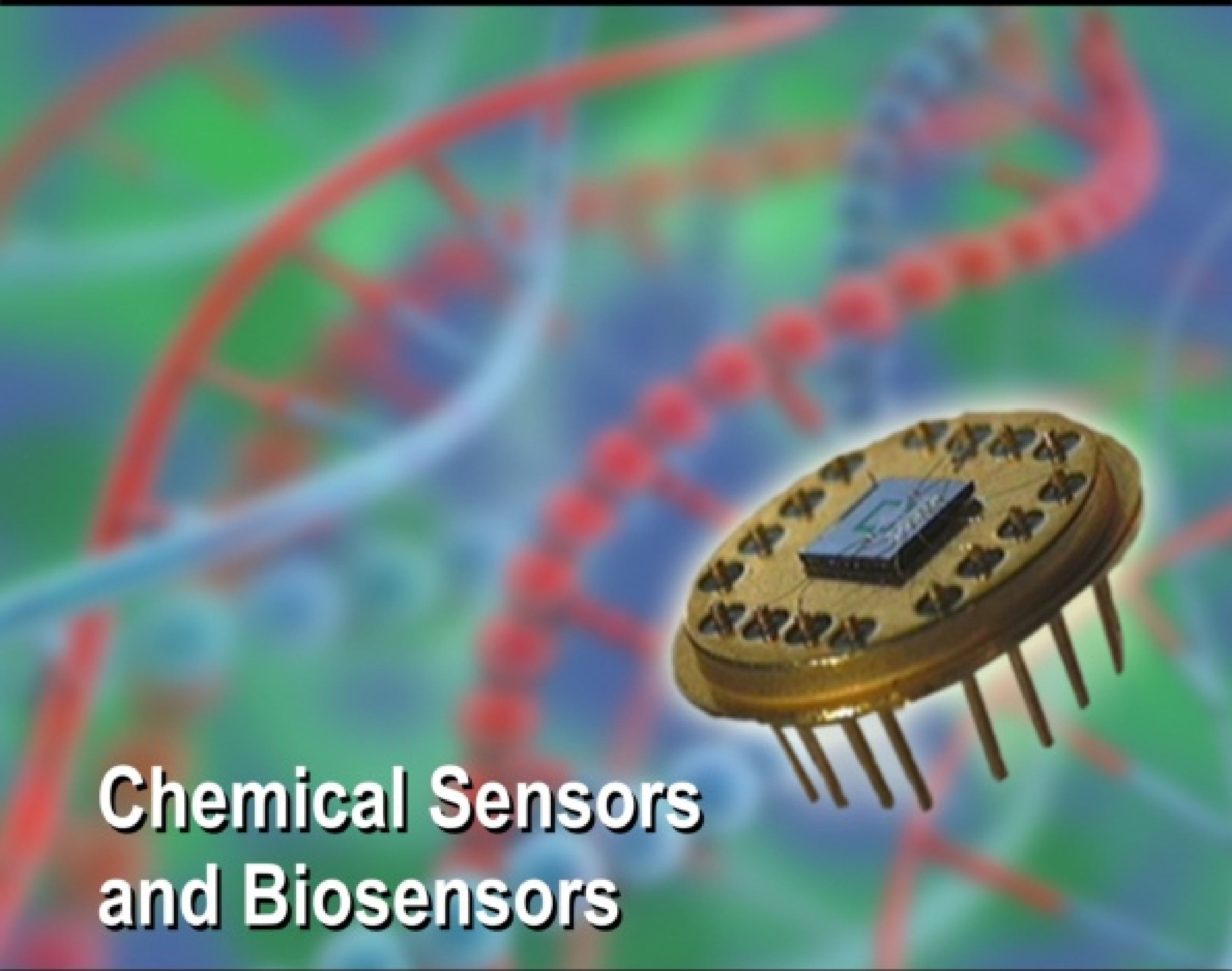

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Sensing Behavior of Sr and Bi Doped $LaCoO_3$ Sensors

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Abstract: Nanosized $LaCoO_3$ (sample S_1), $La_{0.8}Sr_{0.2}CoO_3$ (sample S_2) and $La_{0.8}Bi_{0.2}CoO_3$ (sample S_3) have been synthesized by a sol-gel method using propionic acid and ethylene glycol. It was found that, at 250^0C, sample S_1 shows higher sensitivity for 200 ppm CO gas in air than that for 200 ppm of NH_3. Sensor response for 200 ppm CO gas in air was increased even at 180^0C when tested for sample S_2. Bi doped $LaCoO_3$ (sample S_3) was able to detect 200 ppm NH_3 in air at 200^0C. For both S_2 and S_3, sensor response increases with increase in gas concentrations. The selectivity in gas sensing is proposed on the basis of earlier work and present investigation. *Copyright © 2008 IFSA.*

Keywords: $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$, $La_{0.8}Bi_{0.2}CoO_3$, Sensor material

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1. Introduction

To detect the leakage of poisonous gases released from growing industrial processes, human activities and combustion of fuel, low coast and selective chemical sensors are in great demand. It is well known that, applying some appropriately selected dopants or additives to the base material can enhance the sensitivity and selectivity to a specific gas. Also, the interest is focused on lowering the optimum temperature [1]. Gas selectivity is a matter of great concern, especially when one wishes to detect a test gas in presence of interfering gas. In general, gas selectivity is strongly associated with the receptor function, nature of gas and the semiconductor surface involved. If a target has a specific reactivity to a certain material, it can be used as a gas selective receptor [2]. $LnMO_3$ perovskite-type material (with Ln= rare earth element, M= transition metal) has been attracted the interest of researchers due to their applications as chemical sensors, solid oxide fuel cells (SOFCs) and materials for technology [3-6]. $LaCoO_3$ is p-type semiconductor that has been tested as a catalyst for quite few oxidation reactions [1,7,8] and as a CO gas sensor [9,10]. $LaCoO_3$ have characteristics selective gas adsorption property that bring about a change in electronic property such as change in conductivity and therefore, can be employed as a gas sensing device [11]. Zircona based sensors of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ thin films are reported as CO sensors at 600 and 700^0C in air [12]. Aim of the present work is to study the effect of Sr and Bi as dopants on CO and NH_3 sensing behavior of $LaCoO_3$ compound. A sol-gel method was adopted for preparation of pure and metal oxide doped $LaCoO_3$ nanoparticles. Then we present the sensitivity of these sensors for 200 ppm of CO and NH_3 gases between different temperatures. Following the earlier work and present investigations, sensing mechanism is proposed.

2. Experimental

$LaCoO_3$ compound was obtained through a sol-gel method in order to get fine particles. Nitrates of lanthanum and cobalt in stoichiometric ratio were blended with calculated quantity of propionic acid and ethylene glycol. The mixture was stirred on a hot plate at 80^0C for 2 hr followed by heating at 130^0C for 10 hr. The obtained mass was calcined at 650^0C for 6 hr and labeled as sample S_1. Similar procedures as well as temperature conditions were adopted for preparation of $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Bi_{0.2}CoO_3$ using an appropriate amount of strontium nitrate and bismuth nitrate respectively, with the nitrates of lanthanum and cobalt. The calcined powders of $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Bi_{0.2}CoO_3$ were labeled as sample S_2 and S_3.

Pastes of samples S_1, S_2 and S_3 were obtained by mixing them separately with organic binder. To get thick-films, these pastes were screen printed on alumina substrate provided with two gold electrodes and a heating coil inserted in a tube. On drying, thick films were fired at 500^0C for 2 hr. Before sensitivity measurements, sensors were heated at 100^0C to remove the associated humidity. Sensitivity of samples was tested at different temperatures from $100\text{-}350^0C$.

3. Results and Discussion

Fig. 1-3 show the sensor response of samples S_1, S_2 and S_3 for 200 ppm of each CO and NH_3 in air at different temperatures. While sensitivity measurement, sensor material was kept at different temperatures but test gases were fed into the gas chamber at room temperature. Fig. 1 shows that, the sensor response of sample S_1 is almost same for 200 ppm of both CO and NH_3, although slightly higher response was observed for CO at the same operating temperature. Both gases have a maximum response at an operating temperature around 300^0C.

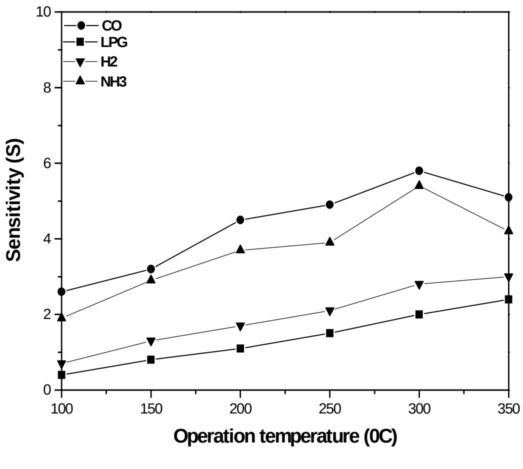

Fig. 1. Sensor response of $LaCoO_3$ element as a function of operation temperature.

Fig. 2 shows the sensor response of sample S_2 at different temperatures. From the plot it is clear that, the sensitivity of material increases for CO and that for NH_3 decreases. The operation temperature for the response was observed at around 250^0C. Following the literature, in formation of $La_{0.8}Sr_{0.2}CoO_3$, strontium ions solubility takes place on a large scale as the Sr^{2+} ions (r=1.16Å) have a similar size to La^{3+} ions (r=1.06Å) [13]. This replacement of ions increases the amount of oxygen vacancies in the sensor material [14] that leads into enhancement of oxygen adsorption and it's conductivity. This could be the reason behind the reduction in operation temperature in sensor response of sample S_2.

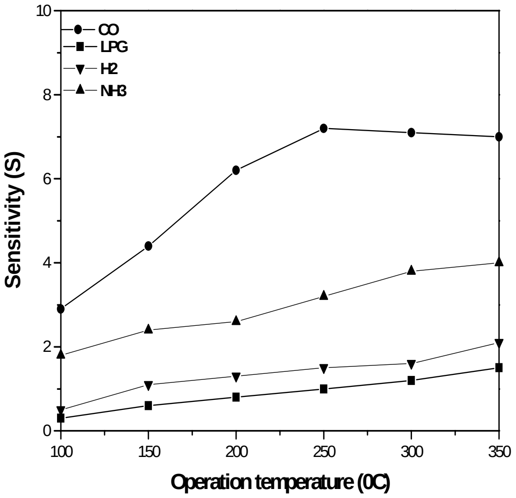

Fig. 2. Sensor response of $La_{0.8}Sr_{0.2}CoO_3$ element as a function of operation temperature.

Fig. 3 shows the senor response of sample S_3 at various temperatures. From figure one can see that, sample is highly sensitive for 200 ppm of NH_3 gas than for CO. The maximum sensitivity for NH_3 gas is shown at 270^0C. This dramatically improved sensitivity of sample S_3 for NH_3 is expected due to difference in oxidation states of dopants viz. Sr^{2+} and Bi^{3+}.

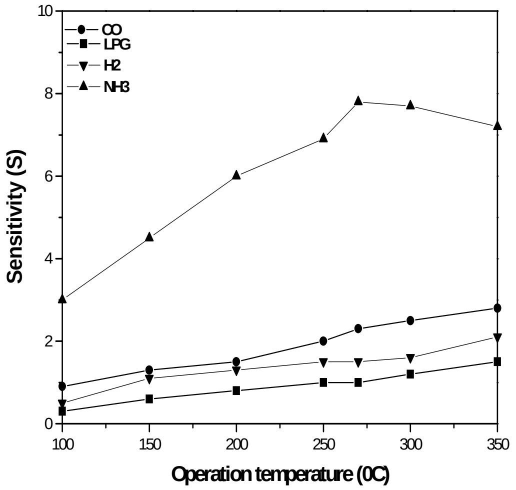

Fig. 3. Sensor response of $La_{0.8}Bi_{0.2}CoO_3$ element as a function of operation temperature.

Fig. 4-5 show sensor response of S_2 at 250^0C and S_3 at 270^0C as a function of CO and NH_3 concentrations (ppm) in air respectively. As seen from figures, for both the samples, response initially increases slowly with increase in gas concentration and then linearly as the gas concentration increases from 200 to 400 ppm.

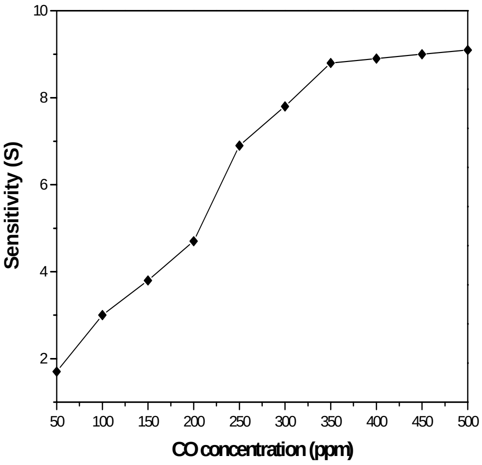

Fig. 4. Sensor response of $La_{0.8}Sr_{0.2}CoO_3$ element as a function of CO concentration at 250^0C.

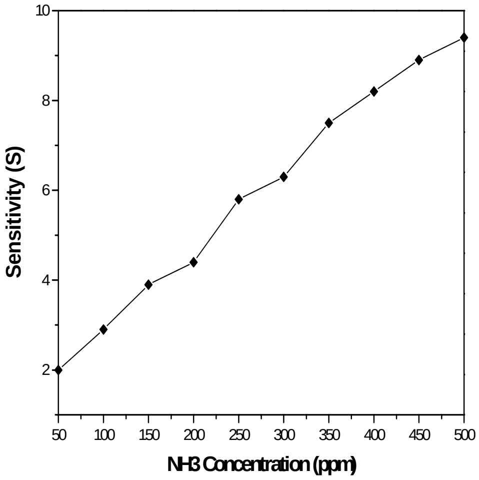

Fig. 5. Sensor response of $La_{0.8}Bi_{0.2}CoO_3$ element as a function of CO concentration at 270^0C.

It is well known that the sensing mechanism of semiconductor gas sensors is a surface controlled phenomenon. At the operation temperature adsorption of oxygen is followed by the formation of oxide species like O^-, O^{2-}, O_2^- etc. (equations 1-2). On the other hand adsorption of test gases, which depends on both the type of test gas and sensor material affect the sensor response. Different reducing gases undergo different reaction processes on the sensor surface. A molecule of CO and NH_3 has a lone pair of electrons. On adsorption, by donating these electrons gases undergo coordination with metal ion from the sensor. Adsorbed molecules of CO or NH_3 reacts with charged oxygen species releasing free electrons (equations 3-4). This forms CO_2 as well as NO_2 gas molecules, which undergo desorption later on.

$$O_{2(ads.)} + e^{-} \rightarrow O_{2(ads.)} \qquad (1)$$

$$O_{2(ads.)} + e^{-} \rightarrow 2O_{(ads.)}^{\;2-} \qquad (2)$$

$$CO_{(ads.)} + O_{(ads.)}^{-} \rightarrow CO_{2(gas)} + e^{-} \qquad (3)$$

$$2NH_{3(ads.)} + 5O_{(ads.)}^{-} \rightarrow 2NO_{2(gas)} + 3H_2O + 5e^{-} \quad (4)$$

However, it is well known that CO is only coordinated with metal ion in lower oxidation state [15]. In comparison with CO, NH_3 can donate its lone pair electron to a metal ion of high oxidation state [16]. In addition to the oxidation state of dopants, the difference in electronic structures of CO and NH_3 should lead to the differences in their adsorption, activation behaviors and in terns the sensitivity of these molecules.

4. Conclusion

The following are the major conclusions made from the above investigation:

1. We have synthesized $LaCoO_3$, $La_{0.8}Sr_{0.2}CoO_3$ and $La_{0.8}Bi_{0.2}CoO_3$ nanoparticles by sol-gel method using propionic acid.
2. $LaCoO_3$ nanoparticles were found to have slightly higher sensitivity towards CO than for NH_3 at around 325^0C.
3. Sr, which is a bivalent metal as a dopant, increases the CO selectivity and sensitivity of $LaCoO_3$ with reduced temperature at 250^0C. S_2 shows fairly good sensing performance to CO gas in the range of 200-300 ppm at 250^0C.
4. Bi; a trivalent metal as a dopant increases the sensitivity of $LaCoO_3$ for NH_3 gas and that for CO decreases. The higher sensitivity of $La_{0.8}Bi_{0.2}CoO_3$ was observed at 270^0C. The sample S_3 shows fairly good sensing performance to NH_3 gas in the range of 200-300 ppm at 270^0C.

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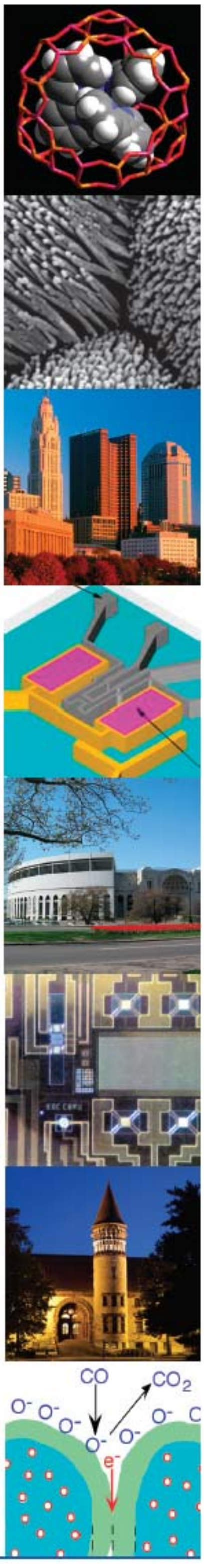

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Meeting Topics

1. Chemical and Biochemical Sensing Technologies
  - Semiconductor sensors
  - Electrochemical sensors
  - SAW and piezo sensors
  - Optical sensors
  - Biosensors
  - Bio-inspired methods

2. Mechanisms, Modeling and Simulation
  - Transduction mechanisms
  - Thin and thick film variants
  - Electrode (material/configuration) effects

3. Emerging Sensing Materials and Technologies
  - Physics & chemistry of new materials
  - Nano-materials and nano-structures
  - Modulation technique
  - Integrated (lab-on-a-chip) designs
  - Smart sensor systems

4. Sensor Arrays and Data Analysis Hybrid Devices
  - Sensor selection
  - Data fusion
  - Numerical modeling
  - Automated calibrations

5. Auxillary Components, Manufacturing and Packaging
  - Preconcentration and catalytic separation
  - MEMS and NEMS
  - Electronics
  - Wireless telemetry
  - Integration with novel non-Si substrates
  - High temperature substrates
  - Device standards

6. Sensing for Health, Safety and Security
  - Sensors for biomedical applications
  - Detection of hazardous chemicals and bio-agents
  - Sensors for environmental and energy security

7. Sensors for Corrosive Processes and Harsh Environment Applications
  - Potentiometric techniques
  - Engineering of built-in sensor modules
  - Building/structure safety sensors
  - Environmental corrosion monitoring –case studies
  - High temperature process monitoring

**8. Business Sense:
Industrial Applications and Markets**
  - Industry presentations
  - Market showcase & specific products
  - Market trends & future needs
  - University-Government-Industry collaboration and networking

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Sensors & Transducers Journal

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.

Topics Covered

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:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

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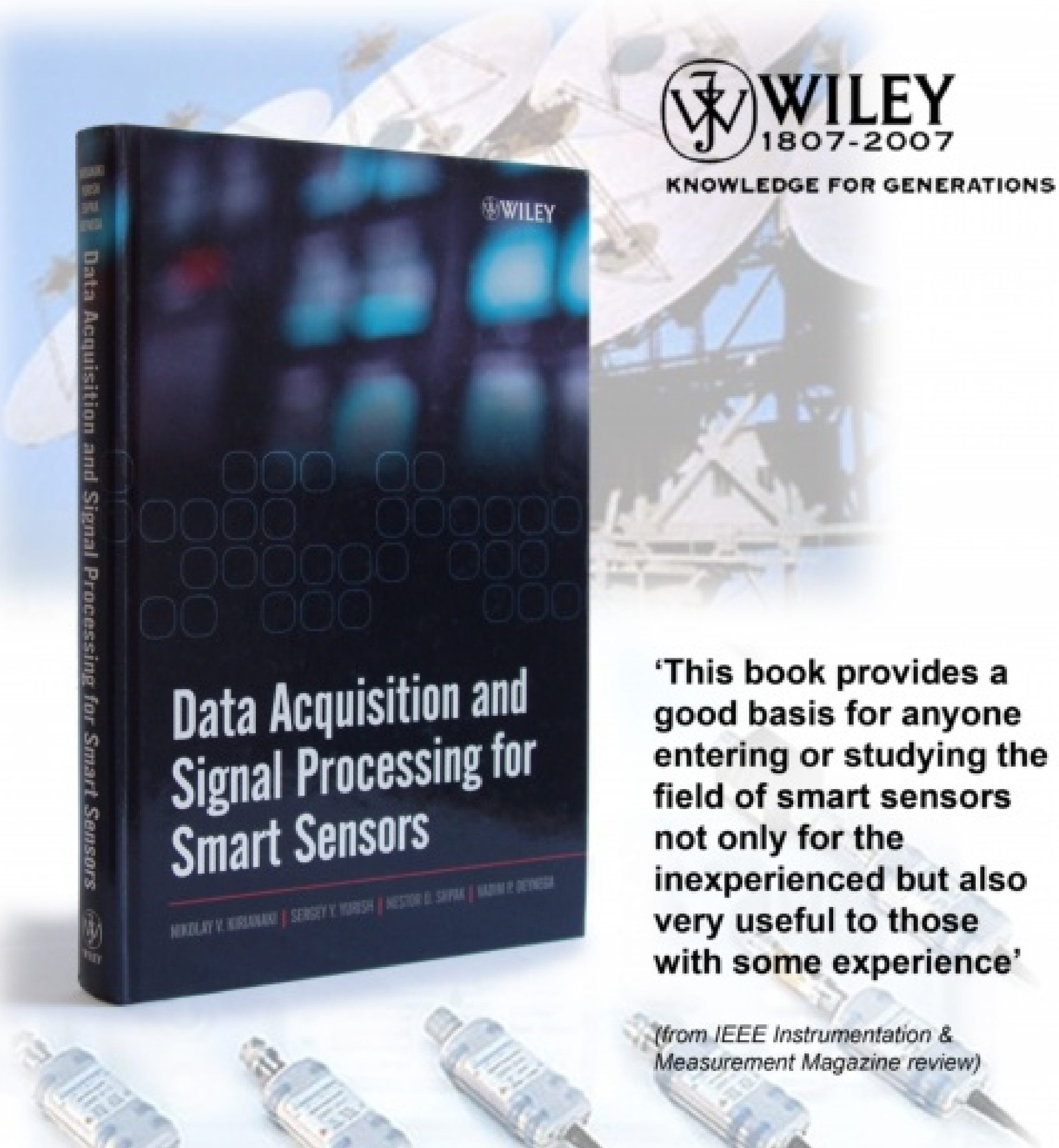
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