Research Proposal for STC

Project Title:

HYDROGEN GAS SENSOR ON PLASTIC SUBSTRATES

Submitted to:

ISRO – IISc Space Technology Cell
Indian Institute of Science
Bangalore 560 012

Investigator(s) from IISc**:** **Dr. VENUGOPAL SANTHANAM**

Co-investigator(s) from ISRO (LPSC): **Dr. NANDAKUMAR K**

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October, 2016
Revised: January 2017

APPLICATION FOR GRANT OF RESEARCH / DEVELOPMENT PROJECT

SECTION –A

1	Title of research/ development Proposal	**Hydrogen gas sensor on plastic substrates**
2	Name of the Principal Investigator Designation and Address	**Dr. VENUGOPAL SANTHANAM** ASSISTANT PROFESSOR, Department of chemical engineering Indian institute of science Bangalore Ph. (O) 91-80-2293 3113 Fax: 91-80-23608120 E-mail: venu@chemeng.iisc.ernet.in Website: http://chemeng.iisc.ac.in/venu
	Name of the Co- Investigator (s) from IISc Designation and Address, Phone, Fax, Email, Mobile Numbers	NIL
	Name of the Co-Investigator(s) from ISRO Designation and Address, Phone, Fax, Email, Mobile Numbers	**Dr. K. Nandakumar** Head, CRD/ PRSG Liquid Propulsion Systems Centre Indian Space research Organisation. Valimala, Thiruvananthapuram-695547 Ph. (0471-2567794 (O) (M) 9496007515 Fax: 471-2567094 E-mail: nandakumar_k@lpsc.gov.in
3	Proposed duration of the research/development proposal	2 years
	Proposed date of commencement of project	April 1, 2017
4	Amount of grant proposed for	**₨ 14,67,400**
5	Department of the institution where R & D project will be carried out	Dept. of Chemical Engineering, IISc
	Other department if any, which will co-operate in this study	
	Details of financial support sought/obtained from other agencies	
6	Specific Aim of the Project	Appendix B (Attached)
	Summary of Proposed research/facilities and objectives (brief statement about the proposed investigation, its conduct and the anticipated results in not more than 300 words)	Appendix B (Attached)
	Key words	Appendix B (Attached)
	Classification of the project	
7	Background and justification (Basis for the proposal with a brief review of the state of the art in the subject, followed by an outline of the rele-	Appendix C (Attached)

	vance and importance of the project, in particular, towards research/development/design related to ISRO programs	
8	Approach (details of the actual approach indicating how each of the objective listed in item 6 (a) will be achieved); deliverables, Task schedule and bar chart	Appendix C (Attached)
9	Previous work done in this or related fields Describe briefly any work done that is particularly pertinent to the proposal & list: (I) your personal publications in this & related areas	Appendix C (Attached)
10	Expected Contributions from ISRO collaborators	Appendix C (Attached)
11	Additional information	Appendix D (Attached)

I certify that a detailed technical report describing the research work/ procedure and its findings will be submitted before the closure of the project.

Date: 28/10/2016 Signature of the Principal Investigator

APPENDIX – A

Project Title:

Hydrogen gas sensor on plastic substrates

Amount of Grant Proposed: **Rs 14 67 400**

Grants (in ₨)	I Year	II Year	Total
(a) Salary # @ ₨ 24000 PM	2 88 000	2 88 000	5 76 000
(b) Equipment⊗	2 50 000	NIL	2 50 000
(c) Working Expenses*	2 50 000	2 00 000	4 50 000
Sub-Total	7 88 000	4 88 000	12 76 000
(d) IISc Overheads @ 15%	1 18 200	73 200	1 91 400
Total	9 06 200	5 61 200	14 67 400
		Grand Total	14 67 400

#Salary for number (specify no. of position) of project associates/project assistants/others

1. Project Assistant: (One) @ ₨ 24 000 PM.

⊗List of Equipments (Give below)

Funding is required for repairing and maintaining FESEM, as well as Air Handling Units. An amount of 2,50,000 is required in the first year for replacing the roughing pump of our FESEM,

***Working Expenses** include Stationary, Consumables and components, chemicals, minor fabrication costs (whichever is needed), TA/DA, etc. (Give a list of important consumable/components with approximate cost).

List of important consumables:

High purity chemicals: - Palladium salts, silver salts (1,00,000), gas cylinders and lab supplies (50,000), flow controllers and fabrication charges for testing facility (1,50,000). AFM tips (50,000), CeNSE usage charges (1,00,000).

APPENDIX – B

Project Title:

Hydrogen gas sensor on plastic substrates

1. **SPECIFIC AIM/ OBJECTIVE OF THE PROJECT:**

1) To fabricate silver@palladium nanostructures on plastic substrates
2) To evaluate the response characteristics and selectivity as a function of different morphologies and nanostructure composition

2. **SUMMARY OF PROPOSED RESEARCH:**

We propose to build on the results of our earlier investigation on silver-palladium alloy nanostructures (ISTC/MCE/VS/286), wherein we had discovered a simple process, using an inkjet printer and galvanic displacement, for fabricating paper/plastic-based silver-palladium alloy nanostructures. Structural and spectroscopic characterizations demonstrated the successful formation of a Pd-Ag alloy upon galvanic displacement. The response of these nanostructures to hydrogen gas indicated that palladium hydride formation with concomitant increase in electrical resistance was the mechanism of sensing. Meanwhile, we have developed a modified process to form silver nanoparticle films with nanoscale gaps. In this project, we propose to optimize a palladium "toning" step to coat these nanostructures and form sub-percolation threshold Ag@Pd nanostructures. Hydrogen gas induced swelling of the palladium coating should help the nanostructure crossover the percolation threshold and result in improved sensitivity and the thin-shell should reduce diffusion times and enable faster response times. The development of flexible hydrogen sensors using a low-cost fabrication process will pave the way for improved safety while handling hydrogen, an issue of growing importance to ISRO as well as the developing fuel cell based 'hydrogen economy'.

Keywords:

Hydrogen gas sensor, Ag@Pd nanostructures, Inkjet printing, Plastic substrates

APPENDIX – C

Project Title: Hydrogen gas sensor on plastic substrates

Background and justification:

Hydrogen carrying pipelines at LPSC span a length of few hundred metres, and represent a significant safety concern. Commercial hydrogen leak detectors are expensive and impose a significant cost burden for continuous monitoring. Moreover, the standard detectors are rigid which limits their ability to monitor joints in pipelines for incipient leaks. Therefore, it is essential to develop a cost-effective, flexible hydrogen sensing platform indigenously.

Available market products mostly rely on catalytic combustion induced temperature changes, thermal conductivity measurements or passivation of surface defects in semiconductor-metal oxide films as the principle of detection of hydrogen [1]. Issues related to cross-sensitivity, reliability and robustness have been addressed by specialised engineering of the sensor, leading to complex designs that are not easily portable or cheap to fabricate on flexible substrates. Metallic films, on the other hand, esp. palladium alloy based resistors have a more specific and selective interaction with Hydrogen under typical sensing conditions and so, can be easily fabricated. Macroscopic palladium films respond to hydrogen very slowly by an increase in resistance [2]. Upon exposure, the surface of palladium metal becomes saturated with dissociated hydrogen, as hydrogen is adsorbed strongly in comparison to other species present in ambient air. The proton then diffuses into the crystal lattice of palladium to from Pd-H_x. The hydride has a higher lattice constant and higher resistivity than Pd. Therefore, the metal swells with an increase in resistance.

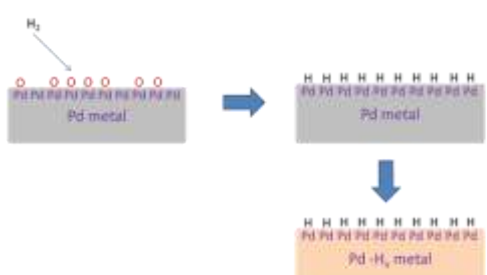

Figure 1: Schematic representation of the various stages of formation of Pd-Hx, when palladium macrostructures are exposed to hydrogen.

The mechanism of formation of Pd-H_x involves saturation of surface of palladium with hydrogen atoms formed by dissociation of hydrogen molecules. Therefore, increasing the surface to volume ratio should improve the sensitivity, while decreasing the size to nanoscale regime would minimize the diffusion timescales to form Pd-H_x and hence vastly decrease the response time of the sensor. Also, the reversibility of the sensor depends on the ability of the sensing film to relieve mechanical stress accumulated during the expansion and contraction cycle without delamination or fracture. Therefore, a mesh of nanoscale - palladium alloy nanostructures would be an ideal platform for manufacturing fast, reversible and robust hydrogen sensors. Palladium mesowires [3], comprising of "beads on a string" morphology, have been fabricated by electroplating on templates from solutions of palladium salt. This architecture when exposed to hydrogen forms Pd-H_x, which swells and closes the nanogap between palladium nanoparticles. This increases the number of percolating pathways resulting in decrease of resistance. The swelling of palladium occurs at the time scale of diffusion of proton into the palladium nanoparticle, viz. < 1s. These devices have fast response, but the fabrication process is prone to large variations leading to irreproducible behaviour amongst sensors. Single palladium nanowires [5] subjected to hydrogen environment respond faster compared to thin films as well as nanoparticle films. However, they cannot be fabricated over a large scale. Palladium metal and alloy nanoparticle films (MPC - monolayer protected cluster films) [4] have been tested for response to hydrogen. The organic capping hinders the access of metallic surface to hydrogen, thus reducing their response. An improvement was sought by ozone and/or thermal treatment of these devices to remove the organic layer. However due to lack of control over the process parameters, the response was irreproducible. Also, Pd-H_x exists in two phases, α and β at low and high H_2 concentrations. These phases have different lattice constant leading to different electrical resistance, thereby leading to a hysteretic behaviour when exposed to cyclic hydrogen concentrations. However, alloying palladium nanostructures with other metals like silver or gold helps to limit hysteretic behaviour [6,7].

Hydrogen gas sensors on flexible substrates have been reported by several groups. These structures can be broadly classified into i) palladium nanostructure decorated carbon nanostructures [8,9] and, 2) palladium thin films deposited on flexible substrates [10,11]. In the former case, carbon nanotubes or graphene are used to provide a flexible and conductuve backbone whose electrical conduction is modulated by the interaction of hydrogen with palladium nanostructures. This interaction is dependent on the morphology of the palladium-carbon interface and thus requires precise control of fabrication, which entails higher costs for controlling the process conditions. In the latter case, thin films are deposited using energy and capital-intensive vapour deposition processes. Hence, in order to produce a robust hydrogen sensor at low-cost for ISRO, we must address the issue of large-scale reliable manufacturing of bare palladium alloy nanostructures with faster response and reliable performance. We propose to use a simple and reliable process based on desktop printing and silver-halide photography to form percolating networks of metallic nanostructures on paper. The conductive nature of the percolating nanostructures shows promise in extending this approach to fabricating wireless RFID antennas [12,13] for remote monitoring of pipeline leaks.

Approach

1) Silver nanostructures will be formed on plastic substrates by using a simple print-expose develop process developed in our group.
2) Different morphologies with different silver loadings will be fabricated,in a systematic manner, and characterized with respect to morphology.
3) Process parameters to fabricate palladium alloy using galvanic displacement or palladium-rich shell using a 'toning' process, will be optimized to form sub-percolation threshold nanostructured films.
4) Finally, electrical characterization of the nanostructured thin films will be performed to determine their sensitivity and detection limits.

Previous work done in this area

Our group has been working in the area of inkjet printed metallic nanostructure formation for the last six years at IISc. Over these years, we have developed and fine-tuned processing parameters to fabricate nanowire networks or nanoparticle morphologies on both plastic as well as paper substrates. These have found applications as RF antennas, strain sensors, flexible electrodes for touch sensing. In our previous STC project we had also characterized the hydrogen gas response characteristics of Pd-Ag alloy nanostructures, fabricated using galvanic displacement.

Facilities Available and Equipment to be procured:

In our laboratory, we have the facility for fabricating metallic nanostructures, and characterizing these using Atomic Force Microscope (AFM), and Field Emission Scanning Electron Microscope (FESEM). We also have access to CeNSE facilities for spectroscopic, material, and electrical characterization of nanostructures.

REFERENCES:

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12. Lee J S, Oh J, Jun J and Jang J, *Wireless Hydrogen Smart Sensor Based on Pt/Graphene-Immobilized Radio-Frequency Identification Tag* ACS Nano 2015, **9** 7783–90
13. Kumar S, Bhat V, Vinoy K J and Santhanam V, *Using an Office Inkjet Printer to Define the Formation of Copper Films on Paper* IEEE Trans. Nanotechnol. 2014,**13** 160–4

Task schedule (Important Milestones for research reviews/completion of tasks – Please indicate Milestones that will be presented at Annual in House Seminar)

1st year: Optimization of protocols for forming sub-percolation threshold Pd-Ag nanostructures. Electrical characterization of fabricated nanostructures.

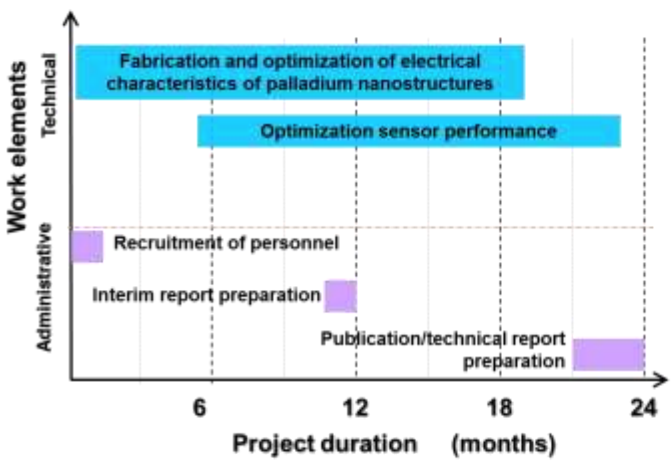
2nd year: Optimization of sensor response to hydrogen gas.

Deliverables (To include the interim and Final Technical report)

1st year: Submission of interim technical report

2nd year: Palladium nanostructure based hydrogen gas sensor on a plastic substrate.
Submission of final technical report

Bar chart of Milestones for listed tasks



APPENDIX – D

1. List of projects (Title/Principal Investigator/Co-investigator/duration/amount) handled previously by IISc PI/Co-PI under STC.

   Nanostructured Chemoresistive Gas Sensor/Dr. Venugopal Santhanam/Dr. K. Nandakumar/2012-14/13.63,200

2. List of publications arising out of these projects

   (a) Journals:

   S. K. Parmar, and V. Santhanam, " In situ formation of silver nanowire networks on paper", Curr. Sci. 107(2), 262-269 (2014).

   S Kumar, V Bhat, K J Vinoy, and V. Santhanam, "Using an Office Inkjet Printer to Define the Formation of Copper Films on Paper", IEEE Transactions on Nanotechnology, 13 (1), 160-164 (2014)

(b) Conference Proceedings:

(c) Technical Reports:

   Nanostructured Chemoresistive Gas Sensor - ISTC/MCE/VS/286 (2014)