INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–8

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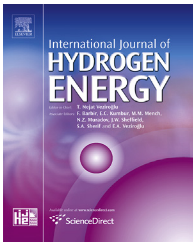

Hydrogen pressure dependent *in-situ* electrical studies on Pd/C nano-composite

P.K. Kulriya [a,*], *Mohit Kumar* [b], *Jitendra Singh* [c], *D.K. Avasthi* [d]

[a] *Materials Science Group, Inter-University Accelerator Centre, Aruna Asaf Ali Road, New Delhi 110067, India*
[b] *Department of Electrical Engineering, Indian Institute of Technology, Jodhpur 342011, India*
[c] *CSIR-Central Electronics Engineering Research Institute, Pilani, Rajasthan 33303, India*
[d] *Department of Applied Physics, Amity University, Noida 201313, India*

ARTICLE INFO

Article history:
Received 20 June 2016
Received in revised form
29 November 2016
Accepted 7 December 2016
Available online xxx

Keywords:
Hydrogen energy
Spillover
Palladium
Nano-composite

ABSTRACT

In present study, the effect of hydrogen gas pressure on the electrical characteristics of the Pd nanoparticle embedded in the carbon matrix was investigated. The structural characterizations of the as-prepared samples were performed using synchrotron radiation x-ray diffraction (SR-XRD), and transmission electron microscopy (TEM). *In-situ* electrical transport studies for high concentration sample showed a slow response time (~30 s) and the resistance versus time curves have similar behavior that of Pd thin films, whereas the lower concentration sample has a fast response time (5 s) along with peculiar response curve. The pressure dependent studies showed that spillover effect was dominant, when samples were exposed to hydrogen gas at low pressure. The superior sensing performance of the lower concentration sample was observed due to extraordinary high surface to volume ratio of nanoparticles as well as good separation provided by the carbon matrix. The spillover effect based hydrogen absorption–desorption mechanism proposed in the present study is important for understanding the hydrogen absorption in the metal nano-composite system and its application in the design of advanced materials for hydrogen gas sensors.

Introduction

Investigations on role of nanoparticle (NP) size, surface and NP-matrix interface on interactions of the metal-hydride system are important for utilization of hydrogen as a clean and renewable alternative to carbon-based fuels. Though, there is a broad range of Pd-based hydrogen sensors which rely on optical and electrical changes on hydrogen incorporation into Pd. However, resistive sensors have advantages such as easy fabrication, stability, low cost, good compatibility with integrated circuits for sensing device fabrication and reproducibility. Few fundamental issues like slow diffusion of hydrogen atom (diffusion coefficient ~ 3.8×10^{-7} cm^2/s) at room temperature leads to large response time, and generation of enormous internal stress leading to peeling off the thick films, limit the use of Pd as an efficient H sensor [1]. Palladium nanostructures seem promising candidate for hydrogen sensing technology due to their high sensitivity and faster response time [2,3]. Pd functionalized Si nano-wire hydrogen sensor showed better sensitivity and faster response time (2.5 s) due to reduction in the electrical conductivity by the depletion of electron at the Pd/Si interface [4].

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* *Corresponding author.*
E-mail address: pawaniuac@gmail.com (P.K. Kulriya).

http://dx.doi.org/10.1016/j.ijhydene.2016.12.026
0360-3199/

Please cite this article in press as: Kulriya PK, et al., Hydrogen pressure dependent *in-situ* electrical studies on Pd/C nano-composite, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2016.12.026

Hydrogen concentration dependent studies on the Pd NP sensor displayed pulse like and saturated response at the higher and lower concentration of H_2, respectively [5]. The response time varied from 5 s (H_2 concentrations >20%) to 30 s (H_2 concentrations < 0.01%) for the sensor fabricated using Pd nano-wire [6]. Chikai et al. reported response time for discontinuous nanogranular Pd film deposited on the top of an amorphous carbon film is about 4 s on exposure to H gas at the pressure of 30 mbar [7]. In summary, enhanced surface area at nano-dimensions, interface, and subsurface sites are important parameters for increasing sensitivity and response time. But, enhanced reactivity of unprotected NP may degrade with time due to reaction of metal with ambient gas molecules; therefore, it is desirable that NP must be embedded in a suitable matrix. Matrix also prevents agglomeration of NP by Vander Waals forces, enhances interaction between surface and subsurface sites, resulting in faster response and higher sensitivity. Matrices such as aluminum oxide, silicon dioxide or immiscible metal matrix have been extensively used for incorporation of metal NPs. But, these matrices are not suitable in case of Pd nanostructures because the Pd may either form alloy or oxidize. Moreover, when Pd NPs were embedded in the insulator matrix possesses very large electrical resistance and cannot be used for gas sensor applications. Therefore, amorphous-carbon is selected as a host matrix for the incorporation of Pd NP, as it has a weak interaction with the metal NPs and does not form alloy with Pd [8]. Carbon materials are also among the best choices for noble metal as catalysts due to their excellent stability in hot water and the easy recovery of the noble metals. Carbon matrix was also used for controlling the surface plasmon resonance properties of the metal-carbon nano-composites systems [9,10]. Recently, C–Pd thin films were also used for selective detection hydrogen in presence of methane [11]. The interaction of the hydrogen with metal supported on carbon is different than free standing metal NPs, and thin films, it is explained by the effect of spillover. First time hydrogen spillover used by *Sinfelt and Lucchesi* to explain the hydrogenation of ethylene due to migration of atomic hydrogen from the SiO_2 supported Pt to Al_2O_3 [12]. In hydrogen spillover, few hydrogen atoms remain attached to the metal, while others diffuse towards the surrounding media which is considered as the primary receptor for atomic hydrogen [7]. Spillover was found to be beneficial for enhancement of the hydrogen storage capacities in the metal-organic system due to hydrogen spillover from a metal catalyst onto the adsorbing surface [13–15]. Hydrogen absorption studies on Pt doped carbon showed that hydrogenation occurred through surface diffusion in a chemisorbed state by the H spillover, while dehydrogenation required diffusion of the chemisorbed species back to Pt [16]. Hydrogen spillover during hydrogen adsorption was also reported for Pt, Ni, Ru and Pd doped carbon [17,18]. However, the detailed investigation is necessary for understanding the mechanism of hydrogen spillover because of the challenging task for the detection of the atomic hydrogen migration in the spillover systems.

In the present study, effect of hydrogen pressure on the spillover of the hydrogen in the Pd/C nano-composite system is investigated by measuring *in-situ* electrical properties of the system. This study is important in the design of the hydrogen gas sensor by the understanding the metal-hydride interaction at the nano-scaled system.

Experimental

Two sets of samples containing Pd in carbon matrix were prepared by atom beam co-sputtering from a graphite target glued with Pd foils in a vacuum chamber at a base pressure of ~10^{-6} Torr [19,20]. Two value of Pd concentration (e.g 25 atomic %, and 45 atomic %, referred as PC25, and PC45) in the carbon matrix, were selected such that its values are below and above the threshold values for the percolation (0.3 vol. %) [21]. Homogeneity across the samples was obtained by rotating the sample holder during deposition. Silicon substrates and TEM girds were used for deposition of nanocomposite (NC) thin films. Hydrogenation of the samples was achieved by exposing them to hydrogen gas at various pressures at the room temperature. The chamber was evacuated using a mechanical rotary pump for deloading of the H_2. *In-situ* electrical resistance measurement setup was used for monitoring the changes in resistance during hydrogen loading and deloading. Resistance between two silver electrodes across the NC thin film was directly measured by an Agilent source-meter. The active area of the device was 5 mm × 10 mm. All measurements were carried out at room temperature (25 °C). As-deposited and hydrogenated samples were characterized using synchrotron radiation powder x-ray diffraction (SR-XRD), Rutherford backscattering spectrometry (RBS), and transmission electron microscopy (TEM). The SR-XRD was performed at the MCX beamline of the Italian national synchrotron Elettra facility in Trieste [22]. The x-ray wavelength (λ) was 1.1223 Å with the x-ray exposure time of 8 s for each diffraction pattern. The XRD data were collected using a NaI(Tl) scintillation detector. The SR-XRD pattern of the as-deposited as well as hydrogenated sample was recorded at a glancing angle of 0.5° in the range of 2θ varying from 20° to 50° with an increment of 0.025°. RBS measurements were carried out to determine the composition and thickness of nanocomposite films. The RBS analysis was performed using 1.7 MV Pelletron accelerator at the Inter-University Accelerator Centre (IUAC) Delhi at normal incidence to the sample surface with collection of the backscattered ions at an angle of 170°.

Results and discussion

Fig. 1 show a representative experimental (black line) and simulated (red line) RBS spectrum for the PC45, and PC25 samples. Fig. 1(a) shows that the plateau regions observed below 1050 keV corresponds to Si substrate. The small hump at energy value of 400 keV and the sharp peak at 1650 keV correspond to carbon and Pd, respectively. As estimated using XRUMP simulations code, the thickness of the film is 125 nm, whereas, concentration of Pd is about 45.0 ± 0.5 atomic% in the carbon matrix [23]. No detectable contamination of oxygen and any other high Z impurities indicating that Pd NPs are well protected and not oxidized. The estimated value of the thickness and concentration thickness for

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