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Ag/Porous Silicon-Based Ammonia-Fed Fuel Cells

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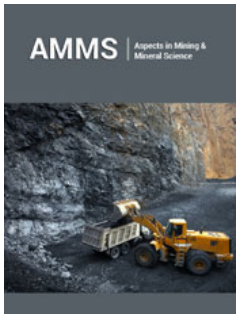

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Abstract

In this paper the results on fabrication technology, structural, luminescent and electrical characteristics of Ag/PS/Si structures as direct ammonia fuel cells are reported. Here nano- Porous Silicon (PS) acts as proton conducting membrane, Ag as catalyst layer. X-Ray Diffraction (XRD), electrical, Photoluminescence (PL) measurements and performance characteristics of Ag/PS/Si cells were studied. Generation of electricity was observed for Ag/PS/Si cells placed in ammonia solution in the range 0-25% at room temperature. Ag/PS/Si cells exhibited the open-circuit voltage of 0.59V and peak power density of 47.2μW/cm^2 with ammonia solution of 25% as fuel at room temperature. Mechanisms of generation of the electricity in Ag/PS/Si cells, exposed directly hydrogen-containing composition as fuel are considered. The advantage of investigated direct ammonia fuel cells consists in simplicity of fabrication technology, which can be integrated into standard silicon micro fabrication and operation of cells at room temperature.

Keywords: Ag/porous silicon/Si fuel cell; Ammonia electrolyte; Power density; Open-circuit voltage

Abbreviations: XRD: X-Ray Diffraction; PEM: Polymer Electrolyte Membrane; PS: Porous Silicon; PL: Photoluminescence

Introduction

A fuel cell is an electrochemical device (a galvanic cell) which converts the energy of a chemical reaction into electrical energy. It usually consists of two electrodes, a negative electrode (or anode) and a positive electrode (or cathode) sandwiched around an electrolyte. In dependence of electrolyte, different types of hydrogen fuel cells have been intensively investigated as the effective sources of clean electric energy. This classification determines the electrochemical reactions, the type of catalysts, the fuel, and the temperature that are required. Several types of fuel cells, depending on the compound used as fuel are now under development, each with its own advantages and disadvantages. It seems attractive to use pure hydrogen as fuel because the products of reaction are heat and water/steam in this case. But the direct use of hydrogen as fuel meets some difficulties. Hydrogen does not exist naturally, and its production and distribution require either, as a liquid, low temperature below -240 °C, or, as a compressed gas, high pressure. Moreover, hydrogen has a low energy density in comparison with other hydrogen-containing compounds such as metal hydrides, ammonia, methanol, hydrocarbons and etc. Polymer Electrolyte Membrane (PEM) cells, known as proton exchange membrane cells, are now considered the leading for automotive applications. PEM fuel cell is a thin, flat, multi-layered "sandwich" and is made up of two electrodes (anode and cathode) surrounded by polymer electrolyte [1]. The rise in portable electronics requires the development of miniature fuel cells compatible with standard silicon micro fabrication technology. Composite materials such as inorganic-organic hybrid materials, often including Nafion®as one of components (Nafion-silica, Nafion-borosiloxane etc.) are the next generation of proton conducting membrane [2,3]. The porous silicon wafer filled with acid or Nafion® was developed as a proton conducting membrane [4]. Porous silicon due to its original structural properties desires to be used in fuel cell structures as a solid "electrolyte". The crystalline structure of porous silicon presents a network of silicon in nano (micro)-regions with an extremely large surface to volume ratio (up to 800m^2/cm^3). The pore surfaces are covered by Silicon Hydrides (Si-H) and Silicon Oxides (Si-O) bonds along which

protons can move [5]. Thus, Porous Silicon (PS) may play the role of proton-conducting electrolyte in porous silicon-based fuel cells. Porous silicon technology can be integrated with the microsystems to be powered [5]. Ammonia provides fuel cells with hydrogen. It contains 17% hydrogen by weight, which can be extracted via thermal catalytic decomposition or electro-oxidation [1]. Although it is toxic, it has a narrower flammable range than hydrogen and is actually considered nonflammable when being transported, whereas hydrogen burns with an invisible flame. Alternatively, ammonia may be oxidized directly in fuel cells without the need for a separate reactor. There are also some significant advantages in terms of storage and transport. Ammonia can be liquefied at room temperature at pressures of 8-10 bar and stored in a similar manner to propane, whereas hydrogen requires expensive cryogenic storage [6]. Ammonia's energy density is (13.6GJ/m^3) much higher than that of hydrogen (3.6GJ/m^3) and comparable to that of Compressed Natural Gas (CNG) and methanol, but lower than gasoline and Liquefied Propane Gas (LPG) [7]. Previous research on porous silicon membrane fuel cells has focused on Hydrogen, Hydrogen sulphide, Carbon oxide [6,8,9], Ammonia [10,11] et.al. In this paper is reported the fabrication details, structural, photoluminescence properties of porous silicon and room temperature performance characteristics of new type direct ammonia fuel cells using proton conducting porous silicon membrane and Ag as catalyst.

Experimental Procedure

Porous silicon layers with thickness of 10-40μm and average porosity from 40% to 70% were prepared on n-type monocrystalline (111) Si substrates with resistivity of 0.45Ω·cm by anodic etching in hydrofluoric-ethanol solution under the white light illumination [6]. For some measurements the PS films were then detached from Si substrate by electro-polishing. The Ag/PS/Si structures were fabricated by evaporation of thin Ag films onto the PS/Si structure at room temperature by using Mo bout in vacuum of 1.3×10^{-3}Pa. The thickness of the deposited silver films (20-40nm) was controlled during the deposition process by Inficon. Electrical measurements of fuel cells were carried out using ammonia solution (NH_3:H_2O) of different concentrations (0-25%). The composition of the ammonium solution changed with the addition of water. Ammonia and water form ammonium hydroxide on the surface of silver:

$$NH_3+H_2O=NH_4OH \quad (1)$$

The crystalline structure of layers was studied by X-Ray Diffraction (XRD) measurements (Bruker XRD D2 PHASER (Germany) Diffractometer in 2θ of 10-70°). Photoluminescence (PL) measurements were performed using PL/PLE/Raman spectrometer (Tokyo Instruments Inc.). The samples were excited by laser beams with a wavelength of 325nm. The current-voltage characteristics, open-circuit voltage (V_{oc}) and short-circuit current density (J) of the Ag/PS/Si cells were measured at room ambient (40% RH) as well as in ammonia solution in measuring cell. The generated by ammonia open-circuit voltage and short-circuit current between the contacts on Ag and Si substrate were measured directly by digital multi-meter (Thurlby-1503). All of the measurements were performed at room temperatures. The photo sensitive properties of the investigated cells were analyzed by measuring current-voltage characteristics in the dark and in daylight. All the cells exhibited weak photosensitivity and therefore ammonia-stimulated measurements of current-voltage characteristics were performed under daylight conditions.

Results and Discussion

Figure 1 shows the dark current density-voltage characteristic of Ag/PS/Si cells. It should be noted that the structures didn't exhibit any noticeable sensitivity under illumination of120mW/cm^2. Therefore ammonia-stimulated measurements of current-voltage characteristics were performed under daylight conditions. For the XRD study, two types of structures, AS/Ag/PS/Si-n (AS-ammonia solution) and Ag/PS/Si-n were fabricated. Both structures were prepared from the same material and the same thickness (n-Si ρ=0.45Om.cm, PS d=15 μm, porosity 48%, thickness of Ag film d=20nm). In case of the first structure three drops of the ammonia solution (25%) were deposited on the surface of the Ag film. Figure 2 illustrates the diffraction patterns of AS/Ag/PS/Si (curve 1, blue) and Ag/PS/Si (curve 2, red) structures. XRD patterns of the sample with a layer of ammonia solution significantly differ from the patterns of the sample without ammonia solution. Common to these structures is the observation of patterns around 28° for (111) plane of porous silicon, 26° and 38° for (210) and (111) planes of silver, respectively. In the sample containing ammonia solution on the surface of Ag are seen a few additional patterns, which are marked by asterisk. The nature of these patterns is not clear yet, but probably they may be associated with some phases of Ag-N-H system on the surface of silver. Figure 3 shows the photoluminescence spectrum of AS/Ag/PS/Si (1-black curve). In the same figure the PL spectra of AS /Ag/Glass (2-red curve) and PS/Si (3-green curve) are given for the comparison. As it is seen from the figure AS/Ag/PS/Si and AS /Ag/Glass structures exhibit the broadband emission around λ=540nm, meantime the PS/Si structure without ammonia solution shows just the broadband emission around λ=700nm, characteristic for porous silicon PL [12]. The nature of emission band around λ=540nm, as well as the additional XRD patterns, which are marked by asterisk in Figure 2 is not clear yet. The presence of λ=540nm emission band in AS/Ag/Glass structure excludes the role of porous silicon in appearance of this band. The most probable origin can be some compound on the basis of Ag-N-H system, responsible for this emission. The well-known Ag $(NH_3)_2$ compound should be excluded, so far as the absorption spectrum of this compound has a maximum at λ=430nm [13]. Figure 4 shows current density-voltage characteristic of AS/Ag/PS/Si cell with 25% ammonia solution as fuel (curve 1). It is seen that AS/Ag/PS/Si cells under ammonia solution produce electricity (the open-circuit voltage V=0.59V, the short-circuit current density 134μA/cm^2 and maximum power density 47.3μW/cm^2 (curve 2) at room temperature. The Ag/Si structure without porous silicon layer showed very little sensitivity to ammonia fuel. Thus, the catalytic layer containing PS plays the main role in the formation of the electrical parameters of fuel cells. The open-circuit

voltage (1) and short-circuit current density (2) of Ag/PS/Si cell with ammonia for different concentrations at room temperature are presented in Figure 5. It can be seen that an increase in the ammonia concentration in the range of 0-25% is accompanied by an almost linear increase in both the open circuit voltage and the short-circuit current density. Thus, the following experimental facts were obtained on research of the electrical characteristics, XRD data and photoluminescence spectrum of Ag/PS/Si-based fuel cells operation with ammonium hydroxide solution (ammonia solution) at room temperature:

A. In the AS/Ag/PS/Si samples containing ammonia solution on the surface of Ag are seen a few additional patterns, which do not belong to components of the structure.

B. In contrast to Ag/PS/Si without ammonia solution, AS/Ag/PS/Si and AS /Ag/Glass structures exhibit the broadband emission a round λ=540nm, which presumably caused by the formation of a new phase in Ag-N-H system.

C. The electricity formation was observed for Ag/PS/Si cells placed in ammonia solution at room temperature. The open circuit voltage and short-circuit current density of Ag/PS/Si cells increase with increasing of the ammonia concentration in the range of 0-25%. The electrical parameters of Ag/PS/Si cells with ammonia solution as fuel are the peak power density 47.2μW/cm^2, the open-circuit voltage 0.59 V and short-circuit current density 134μA/cm^2 at 300K.

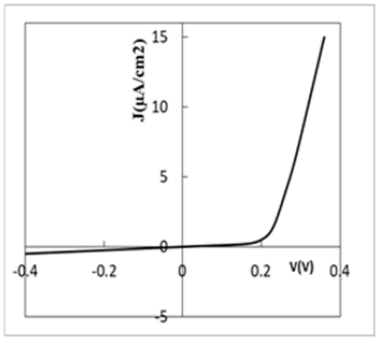

Figure 1: Dark current density-voltage characteristic of Ag/PS/Si cells (300K).

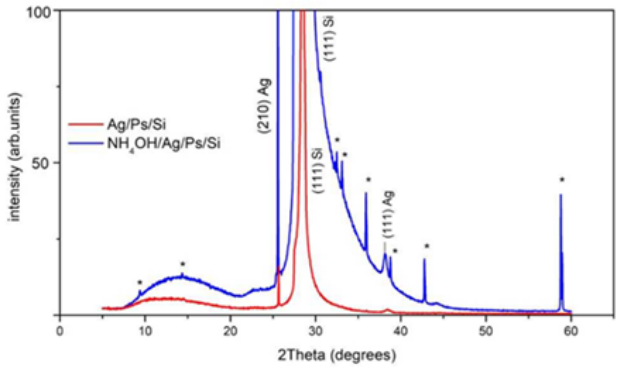

Figure 2: XRD patterns of AS/Ag/PS/Si (1) and Ag/PS/Si (2) structures.

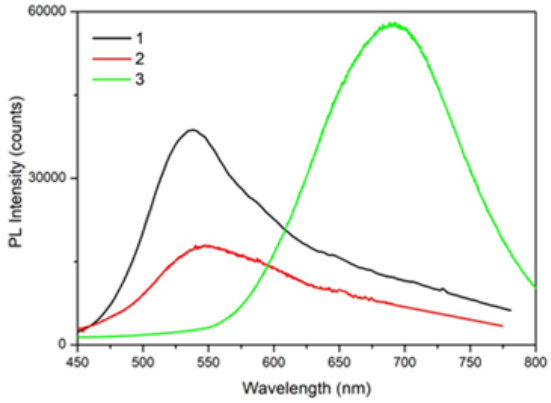

Figure 3: Photoluminescence spectra of AS/Ag/PS/Si (1-black curve), AS/Ag/Glass (2-red curve) and PS/Si (3-green curve) structures.

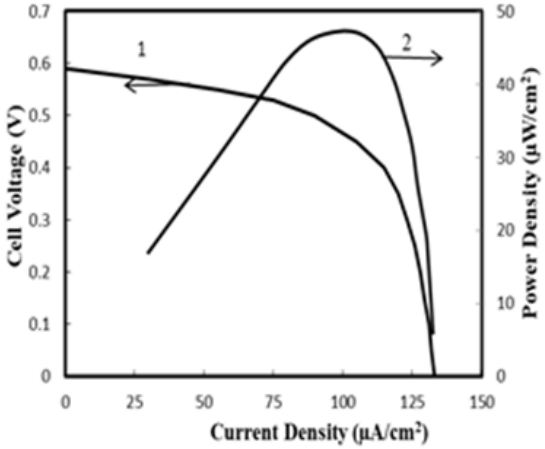

Figure 4: The voltage-current density (1) and power density-current density (2) characteristic of Ag/ PS/Si cells with 25% ammonia solution as fuel (300K).

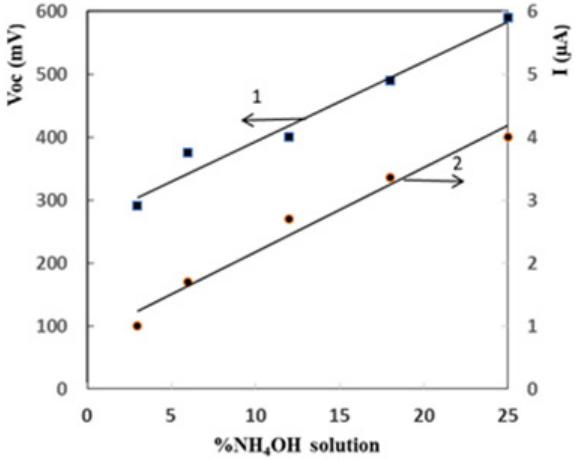

Figure 5: The open-circuit voltage (1) and short-circuit current density (2) of Ag/PS/Si cells versus concentration of ammonia (300K).

The mechanism of electricity generation in the investigated cells under the action of an ammonia solution is similar to the previously proposed generation mechanism for the Au/PS/Si element directly exposed to hydrogen or a hydrogen-containing composition as a fuel [8]. Herewith Ag films play the role of the catalytic anode for Ag/PS/Si cell. The porous silicon acts as proton-conducting membrane and PS/Si interface, which is very imperfect and stressed the role of cathode. Electrochemical reactions proceeding in direct ammonia fuel cell with proton-conducting porous silicon can be expressed as

At the anode: $$Ag + NH_4OH \rightarrow AgNH_4 + OH \quad (2)$$

$$2OH^- \rightarrow 2H^+ + 2e^- + 2O^{2-} \quad (3)$$

At the cathode: $$2H^+ + O^{2-} \rightarrow H_2O \quad (4)$$

Electrons and protons formed in Ag catalyst films as a result of splitting of hydrogen pass through the external circuit and porous silicon layer, respectively, and reach the cathode (PS/Si interface). Here protons recombine with oxygen ions to produce water molecules.

Conclusion

In this study, fabrication and characterization of Ag/PS/Si ammonia fuel cells with porous silicon membrane and Ag catalyst has been presented. The performance of the cell was measured at room temperature with ammonia solution. The test results confirm that the cell generated an open circuit voltages of 0.59V and a power density of 47μW/cm^2 with NH_3 solution as fuel. These results demonstrate the feasibility of development of low-cost Ag/PS-based micro fuel cell for portable electronic application.

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