VERY LARGE SCALE ARRAYS OF CHEMO-MECHANICAL NANO-SWITCHES FOR ULTRALOW POWER HYDROGEN SENSING

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ABSTRACT

We present a novel hydrogen sensor that is based on large arrays of chemically actuated electromechanical nanoswitches, realized by nanogaps in palladium (Pd). An individual switch consists of a trimorph poly-Si/Ti/Pd structure and a fixed Ti/Pd electrode, separated by an approximately 10-15 nm wide nanogap. The volume expansion of Pd at hydrogenation bends the trimorph vertically and creates an electric contact with the electrode. The fabrication process enables the parallel fabrication of many nanoswitches in arbitrary topologies. Hydrogen is detected by current changes up to three orders of magnitude at room temperature and a power consumption of down to pW.

INTRODUCTION

Hydrogen has raised considerable interest as an emission-free energy carrier in fuel cell applications such as hybrid vehicles. However, it is highly flammable between concentrations of 4% and 75% in air and difficult to contain, for what reason sensors for leak detection and monitoring are required.

Most existing H_2 sensors are based on MOS structures using palladium (Pd) gates or continuous Pd wires that exploit the change in threshold voltage or resistivity at hydrogenation, respectively. However, such sensors often require active heating elements for their operation and hence show considerably high power consumption [1].

The first sensors operating at room temperature were based on nanogaps [2, 3]. Therein, the volume expansion of palladium (Pd) at hydrogenation was used to mechanically close nanoscopic discontinuities in thin Pd wires that hence act like switches for electric current. Commonly, sensors based on this effect make use of laterally defined gaps, for instance fabricated by bottom-up techniques such as electrodeposition. The major drawback of these methods is the little control on number and topological arrangement of the nanogaps when aiming for large-scale manufacturing. However, such control by design would be highly advantageous for an industrial application [4]. To this end we developed a concept based on arrays of 2400 nanogaps per sensor with designed topology that can be realized on a wafer scale. The nanogaps are defined out of the wafer plane, which allows the use of thin films for the definition of the gap dimensions. The arrays enable electrical transport by percolation processes and could further be used as an experimental model-system for the study of percolation related effects.

PRINCIPLE AND DESIGN

Palladium is widely used as a sensitive material in hydrogen detectors because of its catalytic surface properties and the ability to absorb vast amounts of atomic hydrogen. The incorporation of H-atoms in interstitial sites in the Pd lattice causes an increase in lattice parameter which in turn results in an external volume expansion of the material. In the present case, this volume expansion is then used to create mechanical contacts between nanometer-spaced Pd interfaces that allow an electric current to pass across.

Since the vertical expansion of a nanometer-thin Pd film on an absolute scale is very small, the lateral expansion of a Pd microstructure is translated into a vertical movement by exploiting the bimorph effect in a multilayer structure.

An individual nanogap is realized as a vertical mechanical switch composed of a trimorph poly-Si/Ti/Pd cantilever and a spatially separated, fixed bottom electrode (Figure 1a). Upon H_2 exposure the Pd layer expands, the cantilever bends and the switch is electrically closed (Figure 1b).

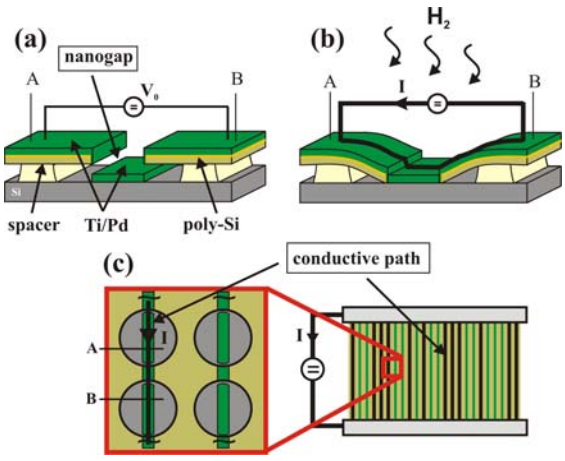

Figure 1 Sensor principle: (a, b) A H_2 induced stress in palladium (Pd) leads to bending of a bimorph cantilever that mechanically connects across a nanogap. (c) An array of nanoswitches allows an electrical current to percolate through the system as a function of the H_2 concentration.

However, the fabrication of single nanoscale switches entails potentially significant process related spread in properties. In addition, the switch-like nature of the structures does not allow a dependence on the hydrogen concentration. By arranging the switches into large arrays, such as parallel linear chains of nanoswitches for example, the electrical transport follows percolation behavior (Figure 1c). Therewith, conduction through the array occurs as soon as a critical number of closed switches - at the percolation threshold - is reached and increases gradually above. The conduction *G(p)* as a function of the number of closed switches *p* in an idealized system of the given topology is given by Ref. [6] and reads

$$G(p) = p^{n_y} n_y^{-1} n_x \qquad (1)$$

where n_y is the number of switches within a single chain and n_x is the number of chains. Percolation theory further predicts that an increasing system size reduces the statistical spread of the system [7].

FABRICATION

The fabrication process is schematically shown in Figure 2. A 50 nm thick poly-Si film is deposited by chemical vapor deposition (CVD) on an oxidized Si-wafer (a). The oxide layer will later serve as a vertical spacer which defines the nanogap size. An array of circular openings is created in the poly-Si by dry etching (b). This pattern is transferred into the SiO_2 by isotropic wet etching using buffered hydrofluoric acid, whereby an undercut of the poly-Si is obtained (c). The nanogaps are created by the use of shadow evaporation of Ti/Pd microwires across the now freestanding poly-Si structures (d).

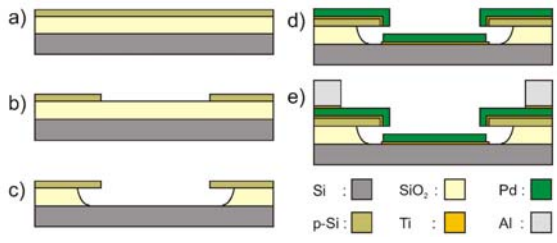

Figure 2 Schematic process flow. Nanogaps are created by shadow evaporation of Ti/Pd microwires across a vertical edge.

The thickness of the metal layers together with the thickness of the oxide spacer thus define the size of the nanogaps which are about 10-15 nm in size. Aluminum electrodes are deposited in a final photolithography, evaporation and lift-off step (e).

The vertical approach allows using relatively simple thin film technology for the nanogaps which is reproducible and uniform over large areas [5] without the need for complex nanolithography. The trimorph structures and the nanogaps are created in the same process step. Figure 3(a, b and c) show respectively optical images of a packaged device, a part of the array structure, and a close-up cross-sectional SEM image of two nanoswitches.

For comparison, two different types of devices were fabricated: A single wire comprising only two nanoswitches in series (one-dimensional system) and a quasi-one-dimensional array of 100 wires in parallel, each containing 240 nanoswitches in series.

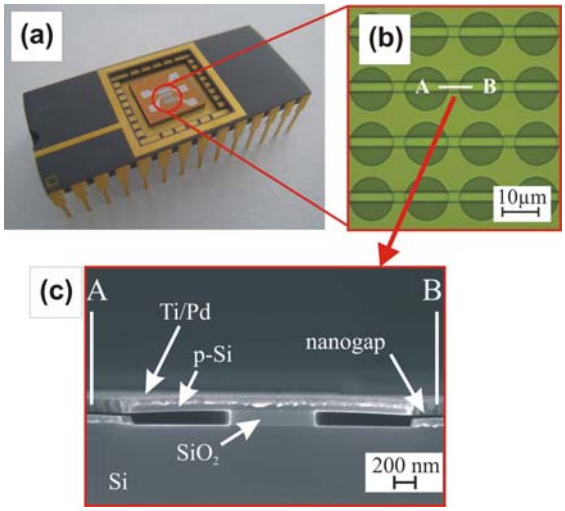

Figure 3 (a) Packaged chip, (b) Array of nanoswitches, (c) Close-up cross-sectional SEM image of two nanoswitches. Estimated gap size: 10-15 nm. Total number of switches: 2400.

EXPERIMENTAL

The sensor chips were glued and wire-bonded into standard dual in-line (DIL) ceramic packages, and placed into a sealed flow cell. Hydrogen/nitrogen gas mixtures were introduced with a constant flow rate and the electrical resistance was measured continuously by a multimeter. No dependence on the gas flow rate and pure nitrogen flow has been observed. This ensured that solely the influence of absorbed hydrogen in palladium is detected.

In Figure 4, a typical response to a 4% H_2/N_2 gas mixture and recovery in air is shown. The

mechanical switching and the resulting electrical percolation processes are completely reversible. Relative changes in electrical current at hydrogen exposure of up to three orders of magnitude are obtained. Values for the electrical resistance in the hydrogenated state, that are around 200 Ω, indicate that the switching mechanism leads to the formation of ohmic contacts. Note that a delay time of some seconds is observed at hydrogen exposure, before the current begins to increase significantly. It is associated with the time that is needed to bend the trimorph structure until a mechanical contact is obtained.

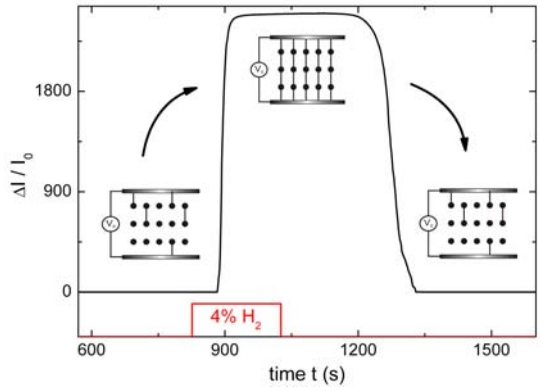

Figure 4 Single sensor response to 4% H_2/N_2 and recovery in air. A relative increase in current of up to three orders of magnitude is obtained by the formation of ohmic contacts. In air, the power consumption is in the range of some pico-Watts.

Further, the sensor response is repeatable without significant drift in baseline and saturation current (see Figure 5). In standby mode (no H_2) the nanoswitches are open. This results in high resistances in the range of some 100s of kΩ up to MΩ, and in an extremely low power consumption in the range of a few pW.

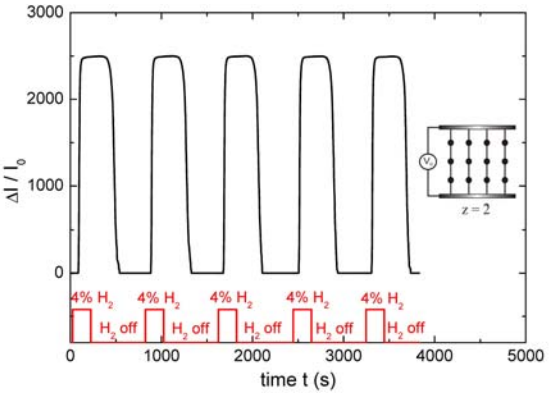

Figure 5 Reversibility of the switching mechanism during hydrogen/air cycling.

Measurements for various hydrogen concentrations revealed different behavior for the single-wire devices and the devices containing arrays of nanogaps. A typical response to hydrogen for a single-wire device is shown in Figure 6. An increase in hydrogen concentration mainly results in a decrease in delay time between the moment of hydrogen exposure and the first significant change in electronic signal. It is explained by the improving kinetic characteristics of hydrogen absorption in Pd. Hence, the trimoph bending occurs within a shorter time period. The slope and the saturation current of the responses remain constant and reflect the switch-like behavior of the structure.

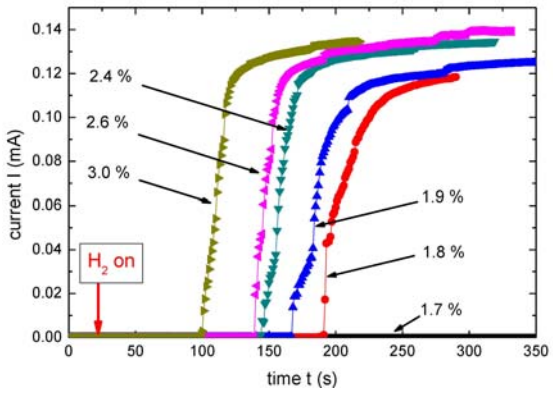

Figure 6 Dependence of the electric current on the hydrogen concentration for a single wire comprising two individual switches.

In contrast, the array structures show a more pronouced dependence of the electronic signal on the H_2 concentration (see Figure 7).

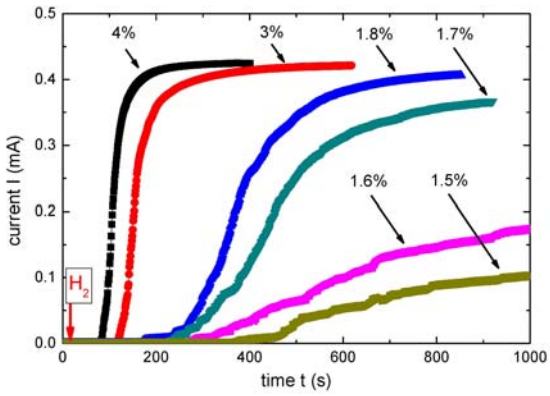

Figure 7 Dependence of the electric current on the hydrogen concentration for a nanoswitch array.

It manifests itself in both a change in saturation current and slope of the current as a function of time. The change in delay time with the hydrogen

concentration shows similar characteristics as for the single wire devices and is hence partly attributed to the change in kinetics of hydrogen absorption.

The pronounced decrease in slope with decreasing concentrations is associated with the network-like arrangement of the nanoswitches and the related transport by percolation. Thereto one can assume that the nanoswitch properties are statistically distributed, caused by process related spread. At low H_2 concentrations, only a fraction of all switches closes, namely the ones that are small enough to bend sufficiently to create a contact at that specific concentration. Since the absorption of hydrogen in Pd decelerates with time, the number of closed switches that contribute to the overall current increases slowly.

For higher concentrations, the critical nanogap-size for closing increases, resulting in a larger number of switches that are involved in the conduction process. Hence, in the early phase of absorption, more switches are activated and bring the system faster over the percolation threshold and to saturation, resulting in a steeper response curve.

Further, the presented sensor concept could likewise be applied to any bi-or multilayer system, wherein an environmental influence induces mechanical stress in one of the layers. Related applications are found in domains such as temperature-, gas- or biosensing. In addition, since the system can be regarded as a generic realization of a percolation network, it could equally serve as an experimental model-platform to experimentally study effects of geometrical and topological constraints in percolation systems.

CONCLUSIONS

In summary, we presented a novel hydrogen sensor concept based on hydrogen actuated mechanical nanoswitches comprising three basic mechanisms: a trimorph effect, the reversible closing and opening of vertical nanogaps and percolation in an interconnected array. The devices detect hydrogen concentrations below 4%, have a power consumption of some pico-Watts in air and show relative changes in signal of up to three orders of magnitude. It was further shown that extended arrays of nanoswitches exhibit different sensing characteristics as compared to small one-dimensional systems.

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