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Linear hydrogen gas sensors based on bimetallic nanoclusters

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ABSTRACT

This work reports on the fabrication of hydrogen gas sensors based on bimetallic palladium-copper nanoclusters. The nanoclusters were generated by sputtering and inert-gas condensation inside an ultra-high vacuum (UHV) compatible system, and self-assembled on an insulating substrate with a pair of pre-formed interdigitated gold/nichrome electrodes. Nanocluster deposition was stopped once their coverage on the substrate reached the percolation threshold. Electrical properties of the fabricated sensors were investigated by means of electrical conductance measurements, and assigned to charge carrier transport within network of metallic islands that is dominated by tunnelling. The produced devices were utilized as conductometric gas sensors. Herein, a constant voltage was applied across the interdigitated electrodes, and the change in electrical current signal was measured which reflects gas concentration. All fabricated sensors showed increase in the conductance upon exposure to hydrogen which can be assigned to the increase in tunnelling current due to the decrease in the size of the gaps between the nanoclusters or the establishment of conducting paths through the network of percolating nanocluster film. The sensors were found to be sensitive at low concentrations of hydrogen at room temperature, and exhibit a linear relationship between hydrogen concentration and the sensitivity. Therefore, those sensors have the potential to be used for practical life applications.

1. Introduction

Hydrogen is an important source of clean energy, and it has many advantages such as: it is pollution free and naturally produced by plants and animals [1,2]. However, the utilization of hydrogen fuel requires reliable hydrogen sensing devices [3]. Among the different types of hydrogen sensors, electrical conductivity hydrogen sensors that utilize nanoclusters as hydrogen sensitive elements were found efficient sensors [4,5]. Herein, the development of hydrogen gas sensors that exhibit a linear response signal with hydrogen concentration, an enhanced response time, and operates efficiently at room temperature is essential [6,7].

In this work we report on the fabrication of conductometric hydrogen sensors based on the change of electrical conductivity upon exposure to hydrogen gas. Each hydrogen gas sensor is formed from a percolating Pd-Cu alloy nanocluster film at the percolation threshold deposited on an insulating substrate with a pair of pre-formed interdigitated electrodes.

Pd-Cu alloy nanoclusters can be formed by various techniques such as: electroless deposition [8–10], sol-gel polymerized [11], and ultrasonic-assisted membrane reduction [12]. However, nanoclusters used in the current work were generated by sputtering and inert-gas condensation from a Pd-Cu target inside an ultra-high vacuum (UHV) compatible system [13–20]. This technique has many advantages over other nanocluster production techniques such as: nanoclusters produced by this technique are of high purity (since they are produced inside an ultra-high vacuum system), the controllability of nanocluster composition, the possibility of nanocluster size selection using a suitable mass filter, and they can be created and self-assembled directly on a desirable substrate [14,19,20]. The present gas sensors may be used in multitude of different applications including, but not limited to, safety sensors, and hydrogen storage devices [4,6,21–24]. For example, hydrogen sensors are used during the hydrogenating cooking oil route, and considered as a cost-effective means to control and quantify the process [25].

2. Experimental

Nanoclusters used for the present work are bimetallic nanoclusters of palladium and copper alloy that were generated by sputtering and inert-gas condensation from a Pd-Cu target inside an UHV system with a base pressure ~10^{-8} mbar [19]. The UHV

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system consists of three main chambers [20]: i) source chamber, ii) mass selection chamber, and iii) deposition chamber (see Fig. 1 in Ref. [19]). The nanoclusters are generated inside the source chamber, travel through the mass filter that enables nanocluster size selection, and then they are deposited on a substrate fixed on a temperature controlled sample holder inside the deposition chamber.

The sputtering and inert-gas condensation process was established inside the source chamber using Argon (Ar) inert-gas. Herein, Ar was used to: i) generate plasma needed to sputter material from the composite target that consists of 33.3% Cu and 66.6% Pd, ii) form nanoclusters by inert-gas condensation of the sputtered material, and iii) enable nanoclusters to travel from the source through the mass filter to the deposition chamber due to pressure gradient between the two chambers. Nanoclusters used in this work were produced using an Ar gas flow rate (f_{Ar}) of 50 sccm and a sputtering discharge power (P) of 62 W. In addition, pure Pd nanoclusters were produced at f_{Ar} = 90 sccm and P = 85 W, and used to produce hydrogen gas sensors for comparison. The sputter head and source chamber were water cooled at room temperature.

A quadrupole mass filter (QMF) was used to determine nanocluster size distribution [18]. The mass filter consists of four parallel metal rods where each pair of opposite rods is connected electrically together to potentials of (U + Vcos (ωt)) and -(U + Vcos (ωt)), where U is a dc voltage and Vcos (ωt) is an ac voltage. For a mass distribution scan, the ratio U/V was fixed and the mass distribution was scanned by varying the frequency, ω. Once the nanoclusters' beam leaves the QMF, it moves through a Faraday cup that detects their current signal, thus, the current signal reflects the number of nanoclusters produced inside the source. The size and composition of the produced nanoclusters were confirmed using a Philips CM10 transmission electron microscope (TEM) and energy–dispersive X–ray (EDX) measurements, respectively.

The percolating gas sensor device was fabricated by depositing the produced nanoclusters on silicon dioxide/silicon (SiO_2/Si) substrates with pre–formed interdigitated gold/nichrome (Au/NiCr) electrodes (formed by standard shadow mask technique) that are 50 μm apart [15]. Nanoclusters were also deposited on SiO_2/Si substrates with pre–formed planer electrodes that are 10 μm apart for electrical conductivity measurements as a function of temperature. The deposition rate of nanoclusters was measured using a quartz crystal monitor (QCM) fixed on a motorized linear translator that enables driving the QCM in front of the substrate, measure the deposition rate, and then drive it back away from the nanocluster beam path. The position of the liner translator holding the QCM could be controlled without venting the system [20].

Fig. 1(a) shows a schematic diagram of the hydrogen gas sensor of the present work. The substrate was mounted on a substrate holder inside the deposition chamber, and connected electrically to a Keithley 238 source measuring unit. The electrical conductance of the sample is monitored during nanocluster deposition while applying a 100 mV voltage across the electrodes. The electrical current signal normally fluctuates at small current values before the onset of conduction due to the deposition of charged nanoclusters on the substrate. Once the percolation threshold is approached, an onset of conduction is observed and the electrical current increases abruptly (see Fig. 1(b)), thus, nanocluster deposition is suddenly stopped using an automatic shutter.

The response of the device to hydrogen gas was characterized inside a temperature controlled a custom-designed Teflon chamber under different concentrations of hydrogen in pure nitrogen or air, as shown in Fig. 1(c) (and Fig. 4 in Ref. [26]). The test chamber was located in a fume hood at atmospheric pressure and 25 °C. The gas flow rate in the sensor test chamber was controlled using Bronkhorst mass flow meters. The response signal of the device was measured using a computer controlled Keithley 236 source measuring unit. A constant voltage of 0.1 V was applied to the sensor, and electrical current signal was monitored as a function of time and gas concentration.

3. Results and discussion

Pd and Cu contents within the produced nanoclusters were found 77 ± 1% and 23 ± 1%, respectively, as measured using EDX. A representative EDX measurement is shown in Fig. 2(a). The lower Cu contents within nanoclusters compared to that in the target is a result of the lower nanocluster production yield of Cu compared to Pd [18]. The size distribution of the produced nanoclusters was measured using the QMF and TEM as depicted in Fig. 2(b) and (c), respectively. The average nanocluster size as measured using the QMF is ~8.1 ± 1.2 nm, where the error is taken as one standard deviation. The TEM image reveals similar average size to that measured using the QMF. The average size of the pure Pd nanoclusters as measured using the QMF is 6.6 ± 0.7 nm.

Electrical conductivity measurement (measured at 1 V) as a function of temperature of $Pd_{0.77}Cu_{0.23}$ nanoclusters deposited on a substrate with planer electrodes at the percolation threshold as shown in Fig. 3. The figure reveals an exponential dependence of the conductivity as a function of temperature. Similar behaviour was observed previously and assigned to charge carrier transport within network of metallic islands that is dominated by tunnelling through small barriers at the junctions between each pair of islands [15,27]. The electrical conductance of such system can be described using [28]:

$$G(T) = \sigma_0(T)e^{\frac{eV}{nk_BT}} \quad (1)$$

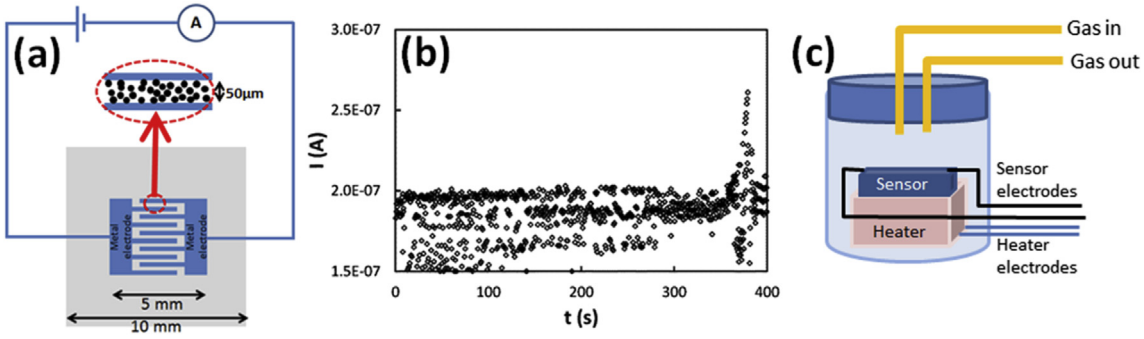

Fig. 1. (a) Schematic diagram of the hydrogen gas sensor formed from a percolating nanocluster film. (b) Electrical current – time dependence of the sensor at V = 100 mV during nanocluster deposition. (c) Schematic diagram of the test chamber.