Supplementary Material (ESI) for Chemical Communications

Nanocrystalline mesoporous palladium activated tin oxide thin films as room-temperature hydrogen gas sensors†

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Electronic supplementary information (ESI)

Experimental:

All chemicals were used as received. Tin (IV) tert-butoxide ($Sn(OBu^t)_4$), palladium acetate ($Pd(CH_3COO)_2$) and solvents (*n*-propanol and i-butanol) were obtained from Aldrich, while the acetic acid was supplied by J.T. Baker. The surfactant Pluronic P123 was donated by BASF Corporation. Compressed gas mixtures of 0.5% vol. H_2-in-N_2, 0.5% vol. CO-in-N_2, forming gas (7% vol. H_2-in-N_2), N_2, CH_4 and compressed air were obtained from Matheson Tri-Gas.

Preparation of sols

2.43 mmol $Sn(OBu^t)_4$ was first dissolved in 12.3 mmol *n*-propanol. To this 0.0583 mmol surfactant dissolved in 16.4 mmol *n*-propanol was added with stirring. A mixture of 9.72 mmol acetic acid in 12.3 mmol *n*-propanol, followed by 14.2 mmol *i*-butanol was added to the above solution with stirring. The stirring was continued overnight (16 h). 0.211 mmol $Pd(CH_3COO)_2$ was dissolved in 22 mmol acetone and added to the above sol with stirring. The doped sol is then filtered through a 0.2 μm GHP Acrodisc® membrane

(Gelman Laboratory) prior to use for coating depositions. For comparison, a PdO-SnO_2 film without surfactant was also prepared. The nominal oxide molar ratio SnO_2:PdO = 92:8 was maintained in the sols. The total oxide (SnO_2 + PdO) equivalent content in the sols was about 5.8% wt. in all cases.

Preparation of films

Homogeneous films were deposited on plasma cleaned silicon wafers, Corning 7059, and silica glass substrates by spin-coating under ambient conditions (room temperature 21±1°C, relative humidity 5-10%), employing a spinning rate of 1,800 rpm. The films were stored in plastic boxes overnight and then dried at 100°C in air. The resulting dried films were then calcined for 6 h at 400°C in air.

Characterization

Refractive index and thickness measurements were made with a J.A. Wollam Co. M44 spectroscopic ellipsometer. All refractive index values (reported at a wavelength of 630.5 nm) and thickness measurements were made in triplicate and averaged. FTIR spectra were taken on a Bruker spectrometer (model Vector 22). XRD was recorded on a Siemens D-500 diffractometer, using a Cu K_α source. TEM was performed on a JEOL 2010 microscope, equipped with an energy dispersive X-ray scattering measurement (EDX) facility. High resolution SEM (FE-SEM) images were obtained in a Hitachi field-emission scanning electron microscope. X-ray photoelectron spectra (XPS) were obtained in a Kratos Axis Ultra XPS using a monochromatic Al K_α X-ray source.

Gas Sensing Measurements

For gas sensing measurements, the films were deposited on SAW substrates. The sensor film was sealed with copper O-ring inside a custom stainless steel holder, having appropriate electrical contacts with the two gold electrodes of the SAW device substrate, and equipped with inlets and outlets for gas flow. A mixture of air, 0.5% vol. H_2-in-N_2, 0.5% vol. CO-in-N_2, forming gas (7% vol. H_2–in-N_2), CH_4 and N_2 was flown over the sensor at a fixed total flow rate of 100 SCCM and P_{tot} = 1 atm, adjusted with the aid of 2 mass flow controllers (Brooks Instr.). The gas relative humidity (R.H.) was controlled by flowing part of the gas through a bubbler filled with DI water. The film's electrical response (resistance range of 30 MΩ and lower) to different gases was recorded with a Hewlett Packard 3478A digital multimeter connected with a computer for data acquisition using LabView software. All dynamic resistance measurements are therefore reported from 30 MΩ to lower values and the data points are collected in every 1 sec of interval. A Techtron® DT-20 multimeter was used to record film resistances manually above 30 MΩ.

Electronic Supplementary Information (XRD results)

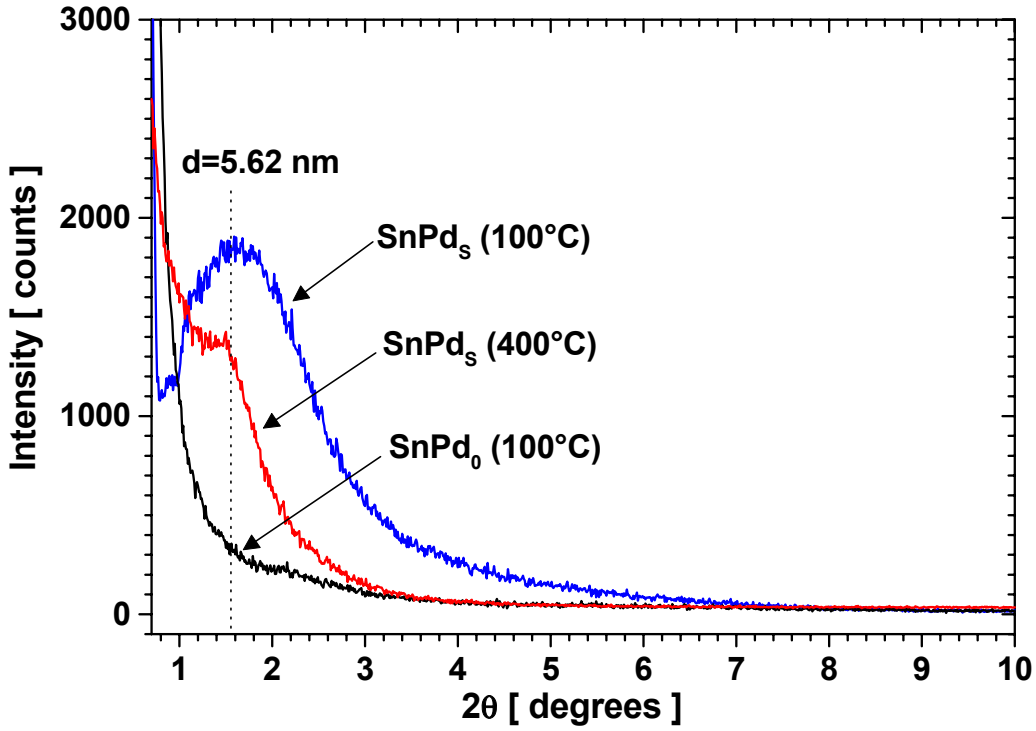

Fig. S1. Low angle XRD of $SnPd_S$ films deposited on Corning 7059 glass substrates. The low angle XRD of the corresponding $SnPd_0$ film prepared without surfactant is also shown.

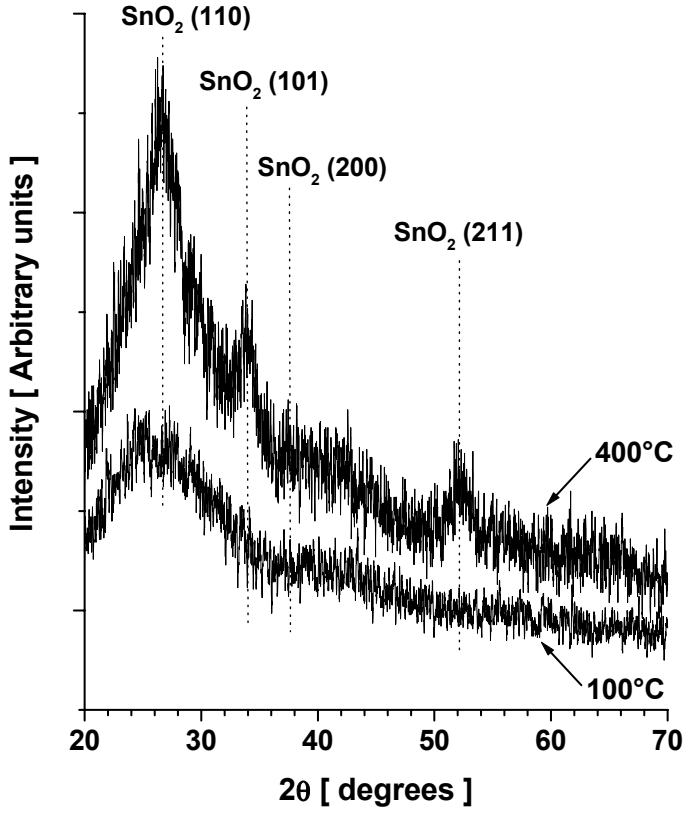

Fig. S2. The wide angle XRD of $SnPd_S$ films deposited on Corning 7059 glass substrates heated at 100 and 400 °C. The 400 °C film shows broad peaks corresponding to cassiterite SnO_2 structure. The SnO_2 (101) peak overlaps with broad amorphous peak arising from the glass substrate.