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A differential capacitive thin film hydrogen sensor

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A compact, differential, hydrogen-specific sensor based on the lattice expansion of $LaAl_{0.3}Ni_{4.7}$ metal hydride thin films has been fabricated and characterized. Characterization of $LaAl_{0.3}Ni_{4.7}$ films performed using a capacitance dilatometer revealed that the lattice expansion was proportional to the partial pressure of H_2 over the range 0.01–1.3 atm used in this experiment. The films were mechanically robust to cycling between vacuum and partial pressures of H_2 up to 1.3 atm and were not poisoned by exposure to atmosphere's containing up to 24% carbon monoxide. A wafer level process has been established for the fabrication of the differential hydrogen sensor which includes both an active $LaAl_{0.3}Ni_{4.7}$ sensing capacitor and an inert Au reference capacitor. A minimum sensitivity of 400 ppm hydrogen is calculated for the differential device.

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1. Introduction

Interest in a hydrogen (H_2) economy, accompanied by intense research to optimize the performance of fuel cells, has underscored the need for low-cost wide dynamic range hydrogen sensors with low false alarm rates. Example applications for hydrogen sensors are leak detection in enclosed environments, monitoring of fuel cell utilization of hydrogen, and the measurement of hydrogen concentration in a reformate stream. There are many commercially available threshold sensors that respond in the low concentration range (<4% hydrogen) suitable for leak detection. However, many of these sensors have issues associated with gas selectivity and robustness to surface contamination. In contrast there are only a few examples of sensors capable of detecting the high concentrations of hydrogen required for fuel cell and reformate gas monitoring and similar selectivity and robustness considerations apply [1–3]. In this paper we discuss a novel hydrogen sensor concept based on the lattice expansion of a metal hydride thin film, that has a wide dynamic range and therefore the potential to meet the demands of a broad range of sensing applications [4,5].

Metal alloys of the formula LaM_xNi_{5-x}, where M can be Al, Fe, Sn, or Co, absorb hydrogen to form metal hydrides reversibly and exhibit a substantial lattice expansion (up to 30%) as a consequence of hydrogen absorption [6]. The magnitude of this expansion leads to decrepitation of the bulk alloy. Addition of the third component (M) to the $LaNi_5$ lattice has been known to reduce decrepitation and Al is particularly attractive for this purpose because $LaAl_xN_{5-x}$ alloys hydride at relatively low temperatures and pressures [7]. Thin films of such alloys are considerably more mechanically robust than bulk alloys [8], due to the lattice expansion being constrained by the underlying substrate. Varying the stoichiometry of the $LaAl_xNi_{5-x}$ alloy allows optimization of the lattice expansion of a thin film while maintaining mechanical robustness. In our experiments this optimum stoichiometry was determined to be $LaAl_{0.3}Ni_{4.7}$.

In this paper, we describe the fabrication and characterization of a differential capacitive device for hydrogen sensing based on the lattice expansion of $LaAl_{0.3}Ni_{4.7}$ thin films. The $LaAl_{0.3}Ni_{4.7}$ film forms one electrode of a simple parallel plate capacitor with an evaporated Au film forming the opposite electrode of the capacitor. The $LaAl_{0.3}Ni_{4.7}$ metal hydride lattice expands on exposure to hydrogen producing a decreased capacitance gap and an increase in measured capacitance. This sensor is ideally suited for hydrogen detection in a variety of environments because the lattice expansion is specific to hydrogen and the temperature and pressure of hydriding can be tuned by varying the alloy composition.

In Section 2, we describe the thin film deposition of $LaAl_{0.3}Ni_{4.7}$ alloys by dc magnetron sputtering and characterization by X-ray diffraction and energy dispersive X-ray fluorescence (EDX). Characterization of the lattice expansion of the $LaAl_{0.3}Ni_{4.7}$ thin films as a function of hydrogen partial pressure with and without water

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Table 1
Deposition parameters for $LaAl_xNi_{5-x}$ films.

Substrate temperature	25–300 °C
Total pressure (Ar)	3–6 mTorr
Substrate RF bias	20–40 W
Ni target power	225–600 W
La target power	50–200 W
Al target power	20–60 W

Table 2
Deposition parameters for $LaAl_{0.3}Ni_{4.7}$ films.

Substrate temperature	200 °C
Total pressure (Ar)	4 mTorr
Substrate RF bias	40 W
Ni target power	450 W
La target power	160 W
Al target power	50 W

vapor and carbon monoxide (CO) is described in Section 3. In Section 4, the process flow for the wafer level fabrication of the sensors and preliminary testing of the complete device is described. In Section 5, the results are summarized and suggestions for further optimization proposed.

2. Material preparation and characterization

Thin films of $LaAl_{0.3}Ni_{4.7}$ were deposited by DC magnetron sputtering on 3 in. Si(1 0 0) substrates in a cryopumped KJL CMS-18 sputter deposition system with a base pressure of 2.6×10^{-11} atm. The system was equipped with four 3 in. magnetrons upon which elemental La, Ni, Al and Pd targets were mounted. Substrates were transferred to the substrate platen in the deposition system through a vacuum load lock. The platen rotated at 20 rpm and the substrate was RF biased during deposition. An Inficon XTM/2 quartz crystal monitor was used for *in situ* calibration of deposition rate after calibration with *ex situ* profilometry measurements. Deposition rates were on the order of 1 Å/s.

Silicon substrates were prepared by solvent degreasing followed by rinsing with a 5% HF solution in a Teflon spinner. The hydrogen passivated substrates were transferred to the vacuum load lock within minutes of this treatment.

Deposition parameters (substrate temperature, source power, pressure and RF substrate bias) were computer controlled and systematically varied over the ranges listed in Table 1. Table 2 lists the deposition parameters for the $LaAl_{0.3}Ni_{4.7}$ alloy for which a large lattice expansion was measured. A few 100 Å of Pd was sputtered on the surface of the film at 50 W to catalyze the dissociation of H_2 and to prevent the films from oxidizing before testing. Films were deposited to a thickness of 2–4 μm.

Films were analyzed by powder X-ray diffractometry and energy dispersive X-ray (EDX) analysis to determine their crystallinity and composition. The EDX measurement was calibrated in reference to a polycrystalline bulk sample of $LaNi_5$. Alloy compositions derived from EDX measurements were accurate to within ±0.1%. All deposition conditions produced polycrystalline films. An X-ray powder pattern of a $LaAl_{0.3}Ni_{4.7}$ film is shown in Fig. 1.

The lattice expansion of 2–4 μm thick $LaAl_{0.3}Ni_{4.7}$ films upon exposure to hydrogen was measured using a tilted plate capacitance dilatometer [9]. The capacitance dilatometer, shown schematically as an inset in Fig. 2, consists of a moveable electrode which rotates on a frictionless pivot. Capacitance is measured as a function of the gap between the moveable electrode and a fixed electrode. The moveable electrode rests on the surface of the $LaAl_{0.3}Ni_{4.7}$ film. As hydrogen is introduced into the system, the film expands and produces an upward force, reducing the capacitance gap between the two electrodes and increasing the capacitance measured. Changes in linear dimension as small as 10 Å have been measured with this type of device.

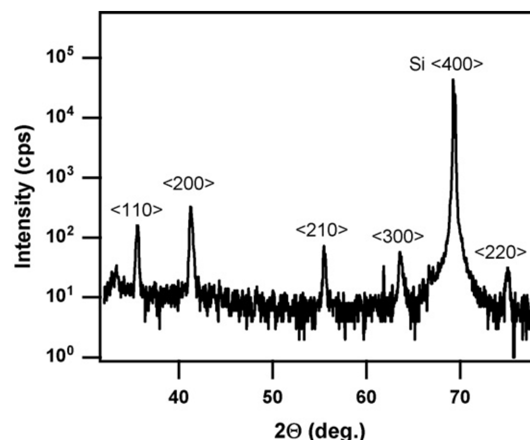

Fig. 1. X-ray diffractometer spectrum of a typical $LaAl_{0.3}Ni_{4.7}$ thin film deposited at temperature T = 200 °C, pressure P = 4 mTorr and RF bias = 40 W.

A schematic of the complete measurement system is shown in Fig. 2. The capacitance dilatometer was mounted inside an O-ring sealed chamber equipped with gas inlet and outlet ports for connection to a gas handling system. The chamber, equipped with a thermocouple, pressure gauge and humidity sensor, was enclosed in a temperature-controlled oven. The gas handling system was controlled by a computer running a custom Labview program for data acquisition and control.

3. Thin film testing

There is a small but measurable change in capacitance due to the dielectric constant of the gas media introduced to the O-ring sealed chamber in which the capacitance dilatometer is mounted. The magnitude of this contribution to the capacitance change (ΔC) for pressures of H_2 and N_2 from 0 to 1.3 atm was measured and is presented in Fig. 3. The dashed lines are least squares fits to the measured data that correspond to ΔC values of $\sim 1.47 \times 10^{-3}$ pF/atm and $\sim 0.88 \times 10^{-3}$ pF/atm for N_2 and H_2 respectively. Accurate measurements of thin film lattice expansion in the dilatometer required that the contribution to ΔC from the dielectric constant of the gas be subtracted from the measured capacitance. The integrated device (Section 4) has a reference electrode that is designed to compensate for the gas dielectric constant contribution to ΔC.

Fig. 4 shows data from a measurement of ΔC upon exposing a 2 μm-thick $LaAl_{0.3}Ni_{4.7}$ film to 0.8 atm of hydrogen at an oven temperature of 78 °C. The maximum capacitance change of ~8 fF reaches 90% of its maximum value in <10 s, comparable to the rate of rise of the measured pressure. We infer from this comparison, that the response time is flow limited and could be inherently faster than τ_{90} = 10 s. The ΔC measured for a bare silicon wafer under the same conditions is plotted for reference (T = 69 °C). In this case, hydrogen does not adsorb on or absorb into the silicon lattice, hence no expansion occurs and the small measured capacitance change (~0.7 fF) is due to the dielectric constant of the gaseous hydrogen only, consistent with the measurements presented in Fig. 3.

The steady state ΔC data, measured after the 10 s rise time, of $LaAl_{0.3}Ni_{4.7}$ films exposed to varying pressures of H_2 at 103 °C are presented in Fig. 5. The data are normalized to the ΔC value measured at 1.3 atm. From these data we can infer that the lattice expansion has a Sievert's type dependence on H_2 pressure ($\Delta C \propto P^{1/2}$) over the range of pressures investigated. We did not observe saturation behavior in the ΔC measurement up to the maximum value of H_2 pressure, 1.3 atm, used in these experiments. This

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