Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 128 (2008) 359–365
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Low-cost electronics and thin film technology for sol–gel titania lambda probes

L. Francioso *, M. Prato, P. Siciliano

CNR-IMM Institute for Microelectronics and Microsystems, Via Monteroni, University Campus, 73100 Lecce, Italy

Received 7 March 2007; received in revised form 20 June 2007; accepted 21 June 2007
Available online 26 June 2007

Abstract

The introduction and clear benefits of silicon technology into automotive application were characterized by fast growth during last years. In effect, the technological innovation of microelectronics carried out a fast revolution into automotive fields, considering physical sensors, gyroscopes, accelerometers and combustion monitoring and air quality control devices. The present paper describes a typical application of the microsystem technology gas sensor products into automotive fields. In particular, the fabrication enhancements of a sol–gel Pd-doped TiO_2 sensor will be investigated. Main advantages of the realized sensors are the reduced dimensions, the low power consumption, and the cheap fabrication process. Some advancements regarding silicon wafer batch production are presented, together with a custom electronic board realized for proportional–integral–derivative (PID) temperature control and digital signal conditioning of sensors signals.

Keywords: Silicon technology; Automotive gas sensors; Metal oxide patterning; PID loop temperature control

1. Introduction

Over the last decades, pressing and dutiful regulations on polluting emissions reduction induced mandatory technological development of engines, which was provided nowadays by electronic regulation of injection and fuel metering, working under optimal conditions in terms of stoichiometric mixture combustion. In relation to the technological development of Otto cycle engines, the scientific research on sensors, which are able to measure the residual oxygen concentrations in the exhaust products of the combustion and assure the stoichiometric working points, started from 1970s under incentive of worldwide engine manufacturers. Microelectronics technologies represent in this field the only possibility of an advanced and intelligent management of different sensors and transducers available onboard of modern vehicles. In effect, the gas sensor scientific community also provided and experimented with different solutions with chemical sensors in order to approach the automotive scenarios [1–4].

The main objective of this paper has been the optimization of deposition techniques by a cheap chemical route like sol–gel with an aim to allow highly reproducible deposition of a Pd-doped TiO_2 thin film at a wafer level on a 3 in. (1 0 0)-oriented DSP (double side polished) silicon wafer; the repeatability of this process was successfully implemented for the fabrication of cheap thin film oxygen sensors for lambda measurements in spark ignition engines, considering also the authors' expertises in thin film micromachining processing [5,6]. The actual cost of a Bosch commercial lambda probe (Model LSF 4.2) with an electronic control unit is about $240 in Italy, while the potential cost is about $120 for a batch production level thin film sensor with an electronics board presented in this work. About the sensitive films, over a total thickness of about 100 nm, it was easy to obtain a thickness spread not larger than 10% over a wafer, considering moreover the possibility to produce approximately 700 devices for each wafer. Optimization phases of physical and interaction properties of thin films with gaseous analytes have been carried out on cheap ceramic alumina substrates, having total surface dimensions of about 4 mm^2; moreover a systematic activity of electrical characterization was carried out in controlled environment and with complex gas mixtures, in order to select materials with better performances for the final validation phase on engine bench scale. All experimental tests in laboratory or on engine benches have been carried out at different working temperatures. The main part of the paper was devoted to a deep engineering of

* Corresponding author.
E-mail address: luca.francioso@le.imm.cnr.it (L. Francioso).

0925-4005/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2007.06.022

sensors in terms of fabrication process and the development of an electronic board that allowed output signal acquisition/digital conversion, and a micro-controller embedded PID algorithm was presented for real-time temperature regulation.

2. Experimental, results and discussion

A sensitive thin film of titania was deposited by a sol–gel method on an alumina substrate (34 mm × 34 mm) composed by a matrix of 225 single devices of 2 mm × 2 mm each and 350 μm thick. The production process was carried out on an entire alumina wafer after preliminary fabrication of backside platinum heaters; finally a UV (ultraviolet) lithography step was performed to obtain interdigitated electrodes onto the sensitive films. Pure TiO_2 sols were prepared in a glove-box with <1 ppm H_2O. Titanium butoxide (2.13 ml) was dissolved in 10 ml of butanol and chelated with 0.64 ml of acetylacetone. After 30 min since the addition of acetylacetone, 0.45 ml of water were added dropwise, obtaining a yellow, clear sol; for the preparation of Pd-doped TiO_2 sols, to a pure sol prepared as above Pd (II) bis-acetylacetonate was added after dissolution in chloroform. The amount of the Pd precursor was such to get a Pd/Ti atomic ratio of 0.05. Thin films were deposited from the previous sols by spin coating onto alumina substrates in a low-moisture atmosphere (about 30% RH), then heat-treating the films at 500 °C in a tubular oven. Two layers were deposited of each material. The sol thus prepared can be employed for deposition of metal oxide sensitive films through the spin-coating technique. The entire synthesis process was carried out in a low humidity atmosphere, in order to avoid fast reactions with the humidity of the atmosphere and subsequent opaque aspect of the resulting films. After the spin coating, the film was dried in air at 60 °C and thereafter calcinated at 500 °C in air for 1 h, to promote removal of residual organic and crystallization of the structure. A detailed schematic of the fabrication process is represented in Fig. 1, described below from left to right, top to bottom of Fig. 1 graphics:

1. Cleaning of an alumina substrate and realization of the first lithography process in order to define the embedded platinum heaters. A positive resist (Shipley S1813, 1.3 μm thickness @ 4000 rpm) was spun onto a substrate at 4000 rpm for 30 s with static dispension. Then a soft baking step was performed on a hotplate at 115 °C for 120 s in order to allow evaporation of residual solvent. At this point we performed the first lithography process to define the platinum heaters by lift-off technique. After development of the resist, an oxygen plasma process was carried out to remove residuals of resist over opened areas of the resist layer. Soon after, the sample was inserted in a sputtering system to perform the platinum deposition, 400 nm thick, in a high vacuum chamber; after the deposition the sample was immersed in an acetone ultrasonic bath to remove all resist layers and leave the platinum layers only on the areas defined by the mask design.
2. Spinning of theTiO_2 precursor onto an alumina substrate at 2000 rpm for 3 s. After the first spinning another layer was deposited to increase the thickness of the sensitive film and reduce the resistivity. Pd-doped titania film sols were spun onto the clean side of an alumina wafer, dried at 70 °C in dry air and then annealed at 800 °C for 1 h in dry air to obtain complete crystallization of structure into a rutile phase revealed by XRD (X-ray diffraction) analysis; the TiO_2 thin film measured about 100 nm of thickness after calcination [7]. The palladium doping procedure modified, optimizing them, the properties of the pure materials, as found for Pt decoration [8].
3. Second lithography step to define the electrical contacts onto the sensitive film, 50 μm width, and 50 μm spaced, and overall active area of 1400 μm × 1400 μm. The procedure was similar to point 1, while previous gold electrodes implemented in this type of combustion sensor were replaced by platinum electrodes that were more stable at higher temperatures than gold (gold diffusion into a sensitive film observed and lack of film's integrity at high temperatures).

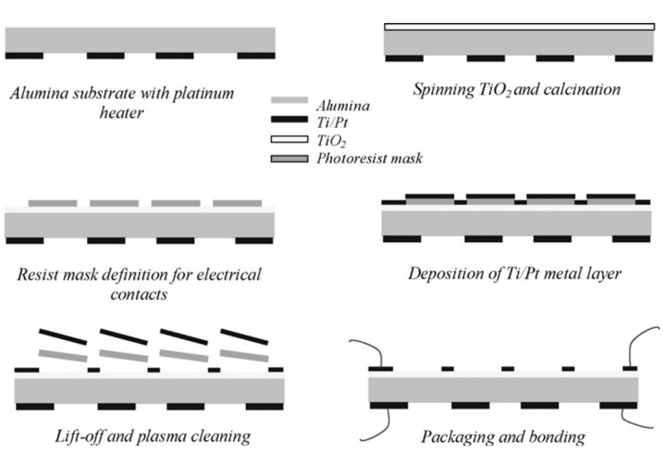

Fig. 1. Fabrication process flow chart for thin film titania lambda sensors.

After these fabrication steps were performed on a single alumina wafer, all single substrates were separated from each other in order to obtain 255 single sensors ready to be packaged onto TO-39 socket.

Fig. 2 depicts the structure of a single sensor after the package step (for better clarity of the picture the structures presented have been realized onto a silicon substrate); the alumina die was bonded onto the socket suspended in air by means of four gold wires that acted as bridges. The structure of the interdigitated electrodes deposited onto a sensitive film, made of platinum, was 50 μm width and 50 μm spaced; the picture detail shows also the dicing saw markers (crosses), necessary for alignment of cutting patterns. The backside of a single device was provided by a platinum heater shaped like a meander to heat the device at working temperature.

Finally, the complete sensor was ready for electrical characterizations in controlled environments and on a real spark ignition engine, as depicted in Fig. 3. Some devices, for experimental purposes, were provided by a steel cap with a topside window to reduce turbulence effects.

An experimental bench was realized in order to perform contemporary data acquisition of a Bosch lambda probe (Model LSF 4.2) and our thin film sensors [9]. The internal combustion