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National Institute for Research and Development in Microtechnologies

\*Retired

## Outline

## Thin Film Technology

Chemical Vapor Deposition Atomic Layer Deposition Sol-Gel Sonochemistry

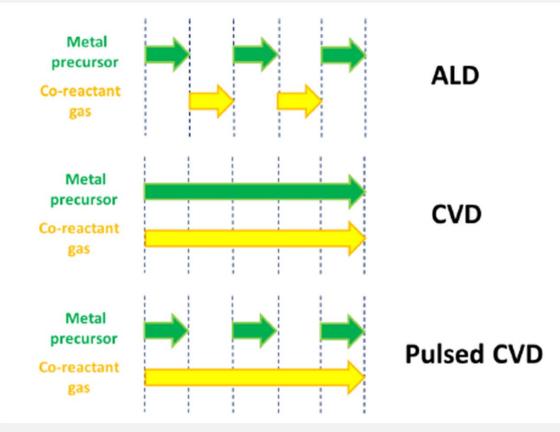
## **Sensor Technology**

Industrial Research Academic Research

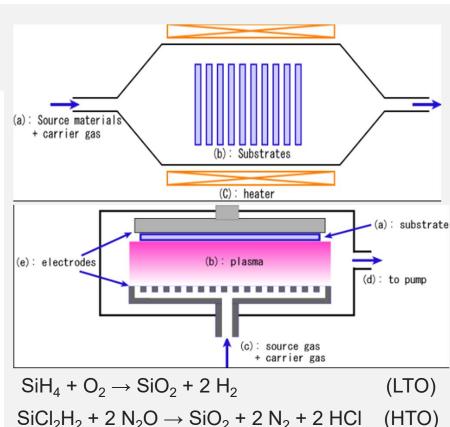
### **Conclusions**

# Chemical Vapor Deposition of Thin Films for Micro-Nanoelectronics

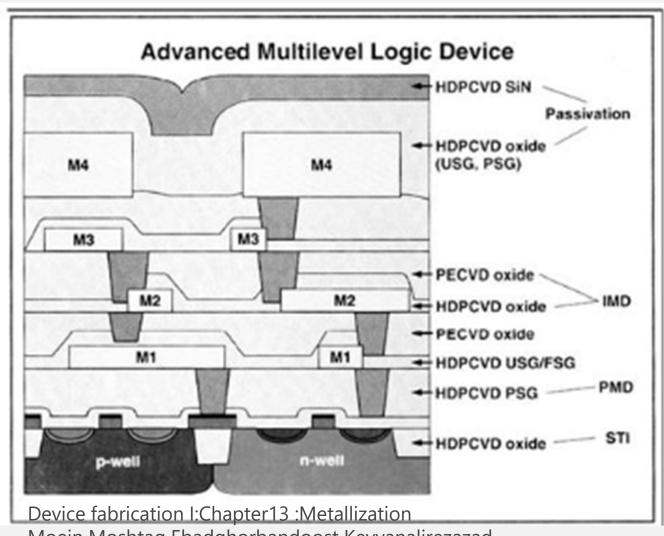
## **CVD Basics**

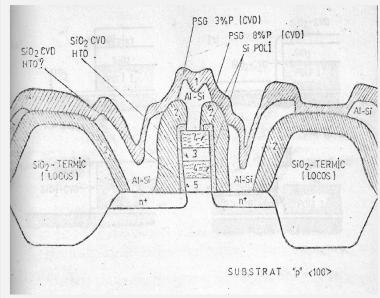


Wang, Xinwei. 2012. Applications of Vapor Deposition in Microelectronics and Dye-Sensitized Solar Cells. Doctoral dissertation, Harvard University.



$$SiH_4 + O_2 \rightarrow SiO_2 + 2 H_2$$
 (LTO)  
 $SiCl_2H_2 + 2 N_2O \rightarrow SiO_2 + 2 N_2 + 2 HCI$  (HTO)  
 $3 SiCl_2H_2 + 4 NH_3 \rightarrow Si_3N_4 + 6 HCI + 6 H_2$   
 $WF_6 \rightarrow W + 3 F_2$   
 $SiH_4 \rightarrow Si + 2 H_2$ 





Cornel Cobianu-Ph.D. Thesis, 1991

Moein Moshtaq Ebadghorbandoost Keyvanalirezazad

# A Theoretical Study of the Low-Temperature Chemical Vapor Deposition of SiO<sub>2</sub> Films

C. Cobianu and C. Pavelescu

1888 J. Electrochem. Soc.: SOLID-STATE SCIENCE AND TECHNOLOGY

September 1983

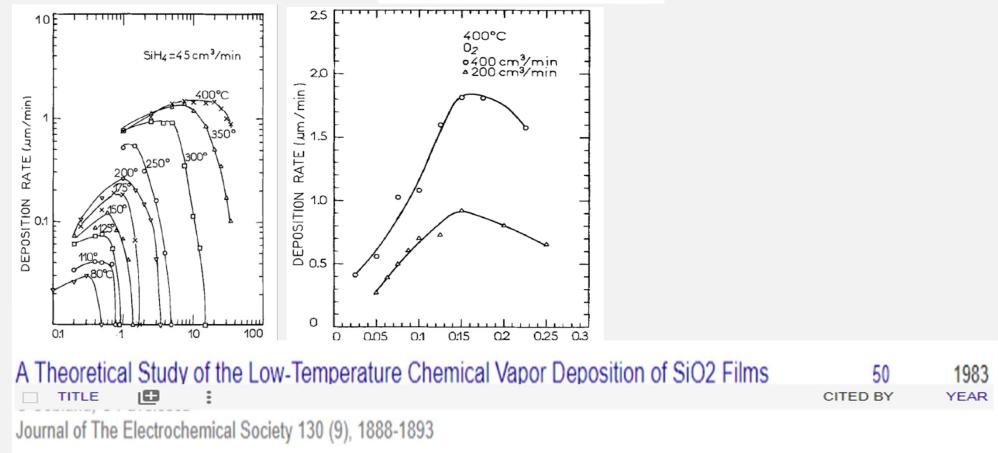
Microelectronica, R-72996, Bucharest, Romania

The silicon dioxide deposition on silicon substrates in the SiH<sub>4</sub>-O<sub>2</sub>-N<sub>2</sub> system was investigated in the temperature range from 80° to 400°C on a nozzle-type reactor at atmospheric pressure. An exponential temperature dependence (of Arrhenius type) with a break at 250°C has been observed for the O<sub>2</sub>/SiH<sub>4</sub> ratio corresponding to the maximum deposition rate and also for the O<sub>2</sub>/SiH<sub>4</sub> ratio corresponding to near-zero deposition rate in the retardation region. Within the bimolecular surface reaction theory (Langmuir-Hinshelwood mechanism), these results are explained, and the break is interpreted as a change in the adsorption mechanism of the reactant gases with temperature. The apparent activation energy of the surface reaction (5.2-6.5 kcal/mol) in the temperature range from 80° to 400°C has been derived from the Arrhenius plot of the maximum deposition rate, in agreement with the above theory. An empirical reaction rate equation has been proposed which, in addition, explains the linear dependence of the maximum deposition rate on silane flow rate at constant O<sub>2</sub>/SiH<sub>4</sub> ratio.

$$v = k_{\rm r} K_{\rm 02} K_{\rm SiH_4} p_{\rm 02} p_{\rm SiH_4} / (1 + K_{\rm 02} p_{\rm 02} + K_{\rm SiH_4} p_{\rm SiH_4})^2$$

## A Theoretical Study of the Low-Temperature Chemical Vapor Deposition of SiO<sub>2</sub> Films





## EFFICIENCY OF THE SiH<sub>4</sub> OXIDATION REACTION IN CHEMICAL VAPOUR DEPOSITION OF SiO<sub>2</sub> FILMS AT LOW TEMPERATURE

Thin Solid Films, 102 (1983) 361–366
PREPARATION AND CHARACTERIZATION

361

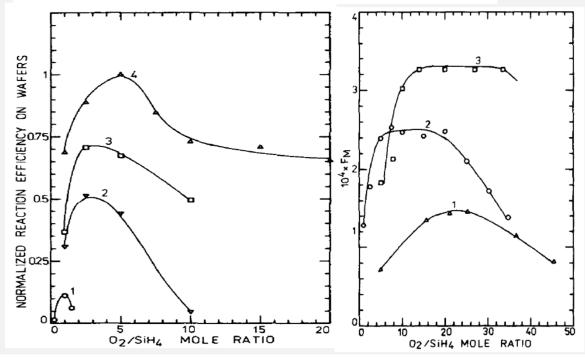
#### C. COBIANU AND C. PAVELESCU

Microelectronica, Str. Erou Iancu Nicolae 34B, R-72996 Bucharest (Romania) (Received August 25, 1982; accepted January 26, 1983)

Our purpose in this paper is to evaluate the efficiency of the  $SiH_4$  oxidation reaction in the heterogeneous low temperature chemical vapour deposition (CVD) of  $SiO_2$  films onto wafers at atmospheric pressure in  $SiH_4$ – $O_2$ – $N_2$  systems as a function of the CVD conditions. We obtained an increase–maximum–decrease type of dependence of the reaction efficiency on the  $[O_2]/[SiH_4]$  mole ratio with temperature as a parameter, in the temperature range 200–400 °C. At a given  $[O_2]/[SiH_4]$  mole ratio the reaction efficiency increases with temperature. These results are qualitatively explained in terms of the bimolecular surface reaction theory and of the dependence of the film density on the CVD conditions. A reactor figure of merit is defined to compare the reaction efficiency on wafers for different CVD reactors.

$$e = \frac{V_{\rm M}}{M_{\rm SiO_2}} \frac{\rho_{\rm SiO_2} v_{\rm d} S_{\rm d}}{F_{\rm SiH_4}} = \frac{V_{\rm M}}{M_{\rm SiO_2}} \rho_{\rm SiO_2} \frac{v_{\rm d} S_{\rm d}}{F_{\rm SiH_4}}$$

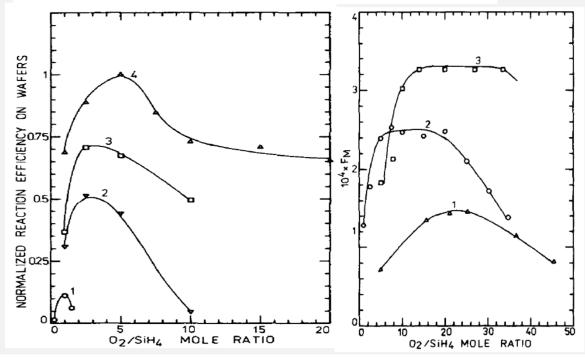
# EFFICIENCY OF THE SiH<sub>4</sub> OXIDATION REACTION IN CHEMICAL VAPOUR DEPOSITION OF SiO<sub>2</sub> FILMS AT LOW TEMPERATURE C. COBIANU AND C. PAVELESCU



Efficiency of the SiH4 oxidation reaction in chemical vapour deposition of SiO2 films at low temperature

C Cobianu, C Pavelescu Thin Solid Films 102 (4), 361-366 27 1983

# EFFICIENCY OF THE SiH<sub>4</sub> OXIDATION REACTION IN CHEMICAL VAPOUR DEPOSITION OF SiO<sub>2</sub> FILMS AT LOW TEMPERATURE C. COBIANU AND C. PAVELESCU



Efficiency of the SiH4 oxidation reaction in chemical vapour deposition of SiO2 films at low temperature

C Cobianu, C Pavelescu Thin Solid Films 102 (4), 361-366 27 1983

# SILANE OXIDATION STUDY: ANALYSIS OF DATA FOR SiO<sub>2</sub> FILMS DEPOSITED BY LOW TEMPERATURE CHEMICAL VAPOUR DEPOSITION\*

C. COBIANU AND C. PAVELESCU

Microelectronica, Str. Erou Iancu Nicolae 34 B, R-72996, Bucharest (Romania) (Received July 7, 1983; accepted May 25, 1984)

The purpose of this paper is to determine the rate constant  $k_r$  of the reaction and the equilibrium constants of oxygen  $(K_{O_2})$  and silane  $(K_{SiH_4})$  adsorption on the surface in the low temperature chemical vapour deposition (CVD) of SiO<sub>2</sub> films from the fit of the experimental dependence of the deposition rate on the CVD conditions to the theory of bimolecular surface reactions.

The results obtained are discussed in terms of (i) an exponential temperature dependence of  $k_r$  with an activation energy of 7.7 kcal mol<sup>-1</sup> and (ii) a temperature dependence of  $K_{O_2}$  and  $K_{SiH_4}$  which involves a transition in the adsorption process of the reactant species from physical adsorption to chemisorption as the temperature is increased over 200 °C.

Silane oxidation study: analysis of data for SiO2 films deposited by low temperature chemical vapour deposition C Cobianu. C Pavelescu

1984

10

Thin solid films 117 (3), 211-216

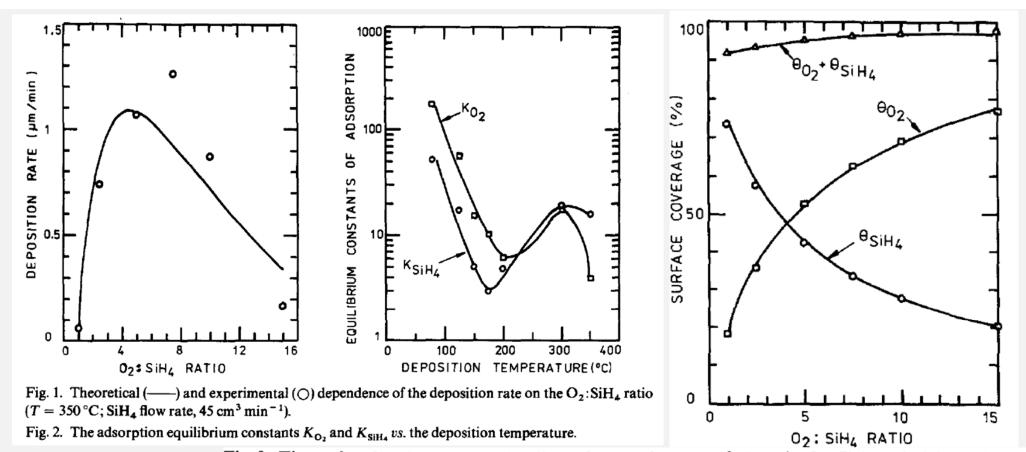
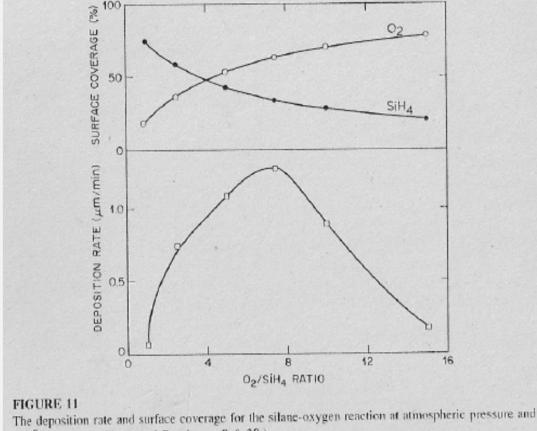


Fig. 3. The surface fractions covered by silane  $(\theta_{SiH_4})$  and oxygen  $(\theta_{O_2})$  vs. the  $O_2$ : SiH<sub>4</sub> ratio  $(T = 350 \,^{\circ}\text{C})$ .

VLSI Technology, S.M. SZE Second edition, 1988

Page 251



350°C. (After Cobianu and Pavelescu, Ref. 28.)

T C Cobianu and C. Pavelescu, "A Theoretical Study of the Low-Temperature Chemical Vapor Deposition of SiO<sub>2</sub> Films," J. Electrochem. Soc., 130, 1888 (1983). 28 C. Cobianu and C. Pavelescu, "Silane Oxidation Study: Analysis of Data for SiO2 Films Deposited by Low Temperature Chemical Vapour Deposition," Thin Solid Fibras, 117, 211 (1984).

# On the Electrical Conduction in the Interpolysilicon Dielectric Layers

Cornel Cobianu, Member, IEEE, Ovidiu Popa, Member, IEEE, and Dan Dascalu, Senior Member, IEEE

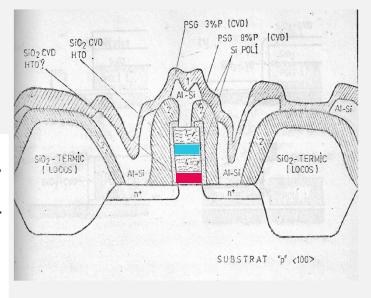
IEEE ELECTRON DEVICE LETTERS, VOL. 14, NO. 5, MAY 1993 213

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O. Popa is with Microelectronica S. A., Str. Erou lancu Nicolae 34 B, Bucharest 72996, Romania, and with the Center of Microtechnology, Str. Erou lancu Nicolae 34 B, Bucharest 72996, Romania.

IEEE Log Number 9208391.

Abstract—Up to now, to reduce the low field electrical conductivity of interpolysilicon dielectrics used in EEPROM devices, the roughness of the poly-SiO<sub>2</sub> interface has been decreased in two ways: 1) by increasing the temperature of oxidation and doping of polysilicon combined with the silicon (undoped or in-situ doped) low-pressure chemical vapor deposition (LPCVD) in the amorphous phase, or 2) by the use of LPCVD high-temperature oxide (HTO) deposited over polycrystalline silicon. In this paper we combine the advantages of each method and present the electrical conduction results of the interpoly structure based on LPCVD smooth surface polysilicon and LPCVD HTO SiO<sub>2</sub>. The data are interpreted in terms of the Fowler—Nordheim mechanism.



On the electrical conduction in the interpolysilicon dielectric layers C Cobianu, O Popa, D Dascalu IEEE Electron Device Letters 14 (5), 213-215

53 1993

### On the Electrical Conduction in the Interpolysilicon Dielectric Layers

Cornel Cobianu, Member, IEEE, Ovidiu Popa, Member, IEEE, and Dan Dascalu, Senior Member, IEEE

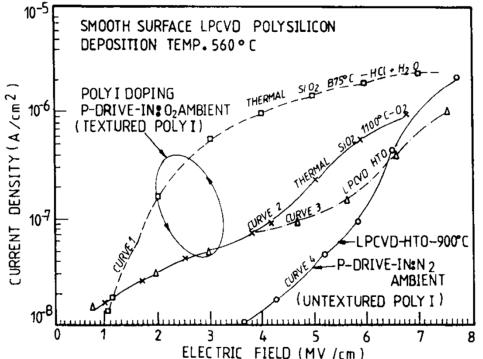


Fig. 1. Current density versus electric field through interpolysiliconstructures with different dielectrics: a) thermal SiO<sub>2</sub> grown on textured poly (curves 1, 2), and b) LPCVD HTO SiO<sub>2</sub> deposited on textured poly (curve 3) or on untextured poly (curve 4).

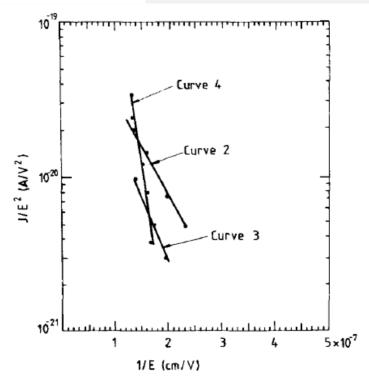


Fig. 2. F-N plots of J-E data from Fig. 1 corresponding to SiO<sub>2</sub> grown at 1100°C on textured poly (curve 2), and LPCVD HTO SiO<sub>2</sub> deposited on textured poly (curve 3) and untextured poly (curve 4). (The same numbers as in Fig. 1 were assigned to the corresponding F-N curves.)

## IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 46, NO. 7, JULY 1999

#### Deposited Inter-Polysilicon Dielectrics for Nonvolatile Memories

## Johan H. Klootwijk, Member, IEEE, Herma van Kranenburg, Pierre H. Woerlee, and Hans Wallinga

Manuscript received October 20, 1998; revised March 8, 1999. This work was supported by the Dutch Foundation for Fundamental Research on Matter (FOM) and the Netherlands Technology Foundation (STW). The review of this paper was arranged by Editor W. Weber.

- J. H. Klootwijk was with the MESA Research Institute, University of Twente, 7500 AE Enschede, The Netherlands. He is now with Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands.
- P. H. Woerlee is with the MESA Research Institute, University of Twente, 7500 AE Enschede, The Netherlands, and also with Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands.

H. van Kranenburg and H. Wallinga are with the MESA Research Institute, University of Twente, 7500 AE Enschede, The Netherlands.

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#### ACKNOWLEDGMENT

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#### REFERENCES

 C. Cobianu, O. Popa, and D. Dascalu, "On the electrical conduction in the inter-polysilicon dielectric layers," *IEEE Electron Device Lett.*, vol. 14, p. 213, 1993.

# Optical properties of silicon thin films related to LPCVD growth condition

M. Modreanu<sup>a,\*</sup>, M. Gartner<sup>b</sup>, C. Cobianu<sup>c</sup>, B. O'Looney<sup>a</sup>, F. Murphy<sup>a</sup> Thin Solid Films 450 (2004) 105–110

aNMRC, Lee Maltings, Prospect Row, Cork, Ireland

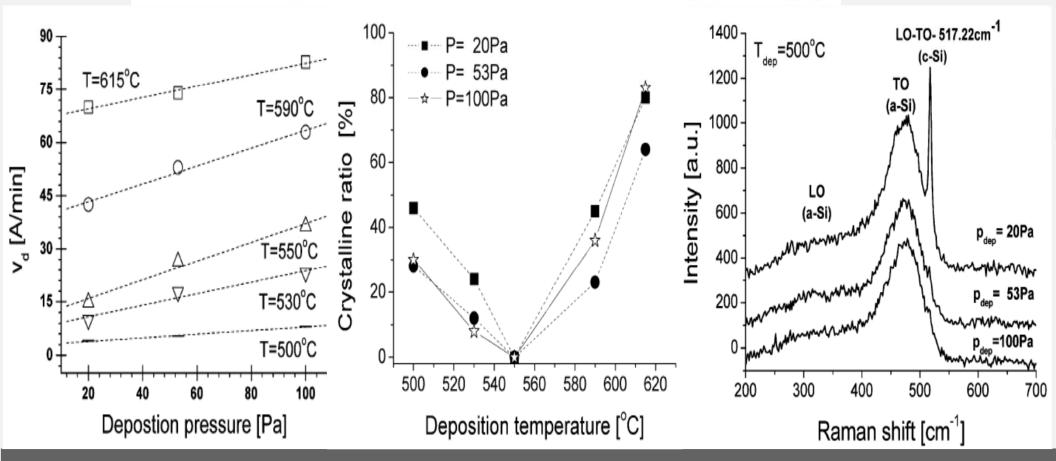
<sup>b</sup>Institute of Physical Chemistry, Spl. Independentei 202, Bucharest 77208, Romania <sup>c</sup>Valahia' Univ. from Târgoviste, P.O. Box 27-17, Bucharest 77550, Romania

In this paper we study the changes in the microstructural and optical properties of silicon thin films produced by the variation of the parameters (temperature and pressure) of the low-pressure chemical vapour deposition (LPCVD) process. Silicon thin films prepared by LPCVD on oxidized silicon substrates over a large range of process parameters ( $T_{\text{dep}} = 500-615^{\circ}\text{C}$ ,  $p_{\text{dep}} = 20-100$  Pa) have been characterized by Raman spectroscopy, spectroscopic ellipsometry (SE), X-ray diffraction (XRD) and atomic force microscopy (AFM) techniques. The phase transition of as-deposited silicon from an amorphous to a crystalline phase via an intermediate mixed phase (few grains in amorphous silicon matrix) can be monitored by the changes in the optical properties and in the Raman spectra. LPCVD parameters, which control the deposition kinetics, are able to influence the optical properties, the structure and/or morphology of the as-deposited LPCVD silicon films. The SE and Raman results prove that it is possible to grow by LPCVD (from pure silane), a silicon film in a (poly)crystalline state at a temperature as low as 500°C.

	TITLE		:		CITED BY	YEAR
Optical properties of silicon thin films related to LPCVD growth condition 30					2004	
M Modreanu, M Gartner, C Cobianu, B O'Looney, F Murphy						
Thin Solid Films 450 (1), 105-110						

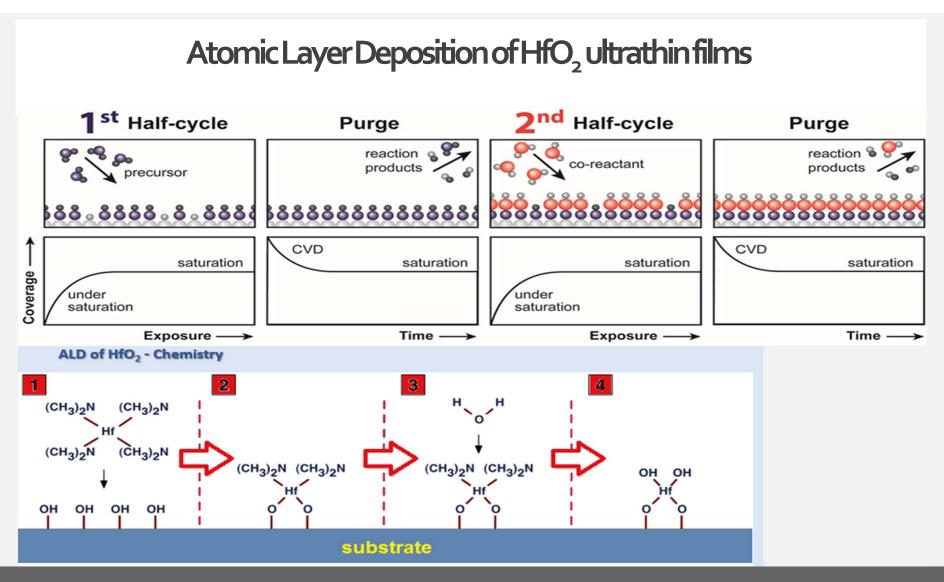
# Optical properties of silicon thin films related to LPCVD growth condition

M. Modreanu<sup>a,\*</sup>, M. Gartner<sup>b</sup>, C. Cobianu<sup>c</sup>, B. O'Looney<sup>a</sup>, F. Murphy<sup>a</sup>



# Atomic Layer Deposition for Nanoelectronics

HfO<sub>2</sub>-High k Ultrathin Gate Dielectrics



# Mechanism of ALD film Deposition from Tetrakis Dimethylamino Hafnium (TDMAH) and H<sub>2</sub>O

$$CH_3 CH_3$$
 $H_3C-N$ 
 $N-CH_3$ 
 $H_3C-N$ 
 $CH_3 CH_3$ 

#### I. HfO<sub>2</sub> ALD on OH-terminated surface

1. 
$$Hf(N(CH_3)_2)_4$$
 half-reaction  
Si-OH\* + $Hf(N(CH_3)_2)_4$  = Si-O- $Hf(N(CH_3)_2)_3$ \*+ $HN(CH_3)_2$   
Si-O- $Hf(N(CH_3)_2)_3$ \* + Si-OH\*=Si-O- $Hf(N(CH_3)_2$ \* +  $HN(CH_3)_2$ 

2. Water half-reaction Si-O-Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>\* + 2H<sub>2</sub>O=Si-O-Hf-(OH)<sub>2</sub> + 2HN(CH<sub>3</sub>)<sub>2</sub>

#### II. HfO<sub>2</sub> ALD on H-Terminated Si Surface

1.  $Hf(N(CH_3)_2)_4$  half-reaction Si-H\* +  $Hf(N(CH_3)_2)_4$ =Si-Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub>\*+HN(CH<sub>3</sub>)<sub>2</sub> Si-Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub> +Si-H\*=Si-Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>\*+ HN(CH<sub>3</sub>)<sub>2</sub> 2. Water half reaction

Si-Hf(N(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>\*+2H<sub>2</sub>O=Si-Hf-(OH)<sub>2</sub> + 2HN(CH<sub>3</sub>)<sub>2</sub>

## Silicon Wafer-Cleaning Process

RCA-1: 5 parts DI-H<sub>2</sub>O+1 part 27% NH<sub>4</sub>OH + 1 part 30% H<sub>2</sub>O<sub>2</sub>

-Remove organic residues from Si surface

-Leaves an ultrathin SiO<sub>2</sub> film on the Si surface

RCA-2:6 parts DI-H<sub>2</sub>O + 1 part 27% HCl + 1 part 30% H<sub>2</sub>O<sub>2</sub>

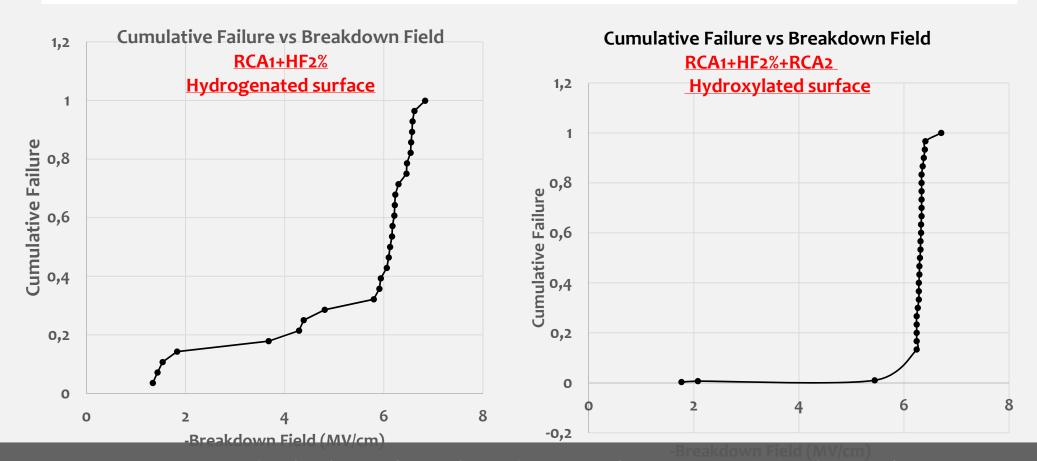
-Removes metal ions from silicon surface

-Leaves an ultrathin SiO<sub>2</sub> film on the Si surface

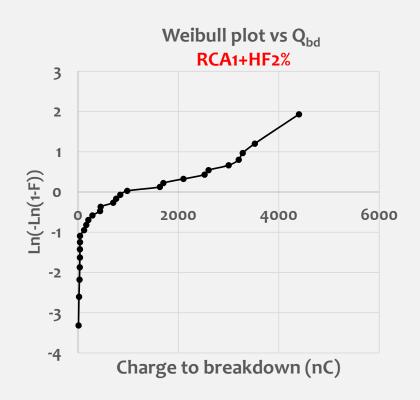
Cleaning processes: RCA1+ HF2%: H-terminated silicon

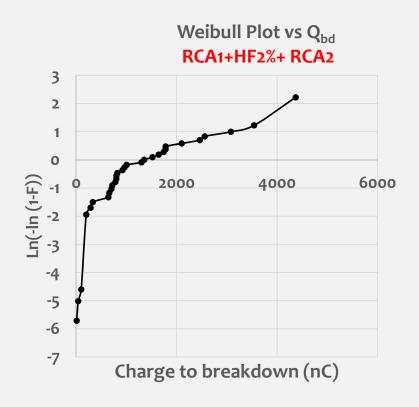
RCA1-HF2%-RCA2: OH-terminated silicon

# Comparison of the Cumulative Failure Distributions vs Breakdown Field HfO2 films



## Comparison of Weibull Distribution vs Qbd





#### ELECTRICAL PROPERTIES OF AS-DEPOSITED ALD HfO<sub>2</sub> FILMS RELATED TO SILICON SURFACE STATE

Cornel Cobianu<sup>1,2</sup>, Florin Nastase<sup>1,2</sup>, Niculae Dumbravescu<sup>1,2</sup>, Octavian Buiu<sup>1,2</sup>, Adrian Albu<sup>1</sup>, Bogdan Serban<sup>1,2</sup>, Mihai Danila<sup>1</sup>, Cosmin Romanitan<sup>1</sup>, Octavian Ionescu<sup>1,2</sup>

#### CAS 2018 PROCEEDINGS

National Institute for Research and Development in Microtechnologies-IMT Bucharest, Romania.

<sup>2</sup> Research Center for Integrated Systems, Nanotechnologies and Carbon-Based Nanomaterials (CENASIC)-

Abstract-In this paper, we present an experimental study of the electrical properties of the as-deposited HfO2 films obtained by atomic layer deposition (ALD) method from tetrakis dimethylamino hafnium and water vapors at 200°C as a function of the silicon substrate preparation, in terms of Si-H and Si-OH terminated surfaces. High frequency characteristics have proven that relatively higher effective dielectric constant, lower fixed charge at the Si-HfO2 interface and lower oxide trapped charge were obtained on MOS capacitors with HfO2 dielectric performed on Si-OH terminated Si surface with respect Si-H terminated surface, proving a more robust Si-O-Hf interface with respect to Si-Hf-O interface.

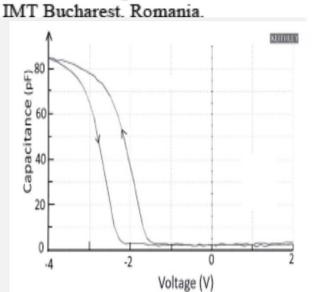


Fig. 1. High frequency (1 MHz) C-V plot of a MOS capacitor having as-deposited ALD HfO<sub>2</sub> film deposited on Si-H terminated silicon (p type) and Al gate, annealed in N<sub>2</sub> at 250°C.

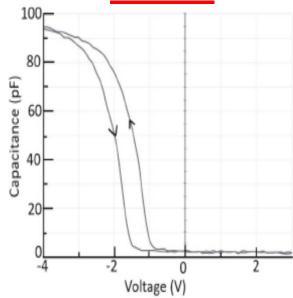
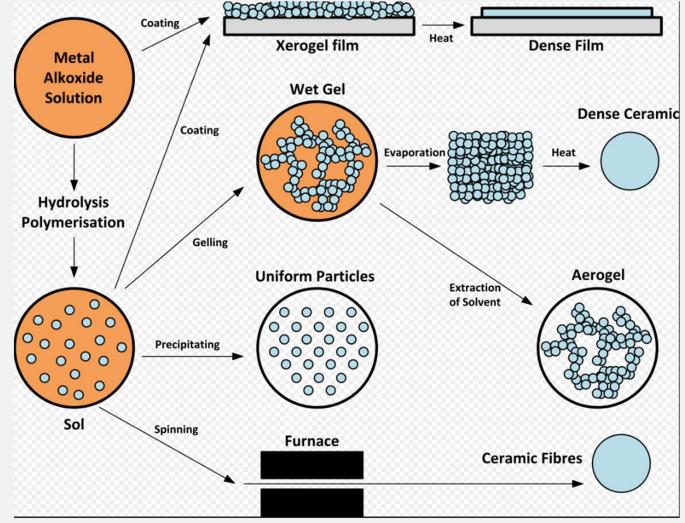


Fig. 2. High frequency (1 MHz) C-V plot of a MOS capacitor having as-deposited ALD HfO2 film deposited on Si-OH terminated silicon (p-type) and Al gate, annealed in N<sub>2</sub> at 250°C





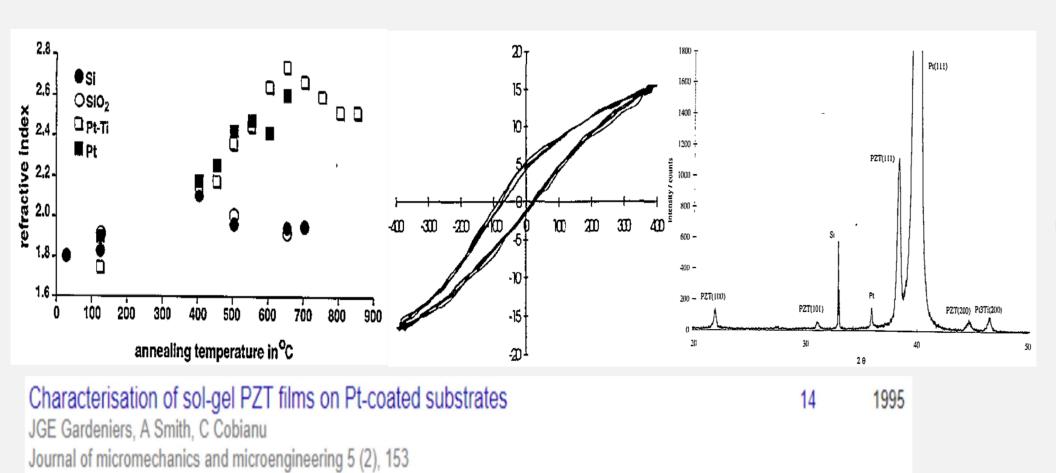
C.J. Brinkler and G.W. Scherer, "Physics and Chemistry of Sol-Gel Processing" 1990

# Characterization of sol-gel PZT films on Pt-coated substrates

J G E Gardeniers†, A Smith† and C Cobianu‡ J. Micromech. Microeng. 5 (1995) 153–155. TEMPUS Project -1993

- † Micromechanical Transducers, MESA Research Institute, PO Box 217, NL-7500 AE Enschede, The Netherlands
- ‡ Institute of Microtechnology, PO Box 38-160 Bucharest 72225, Romania

**Abstract.** A conventional sol-gel process was used to spin-cast PZT films on oxidized Si wafers coated with sputtered Pt layers. After annealing at  $550\,^{\circ}\text{C}-800\,^{\circ}\text{C}$ , the resulting perovskite-type PZT films showed different textures and surface morphologies, depending on whether or not a Ti adhesion layer was used. If a Ti layer was present, Ti diffusion into and through the Pt film leads to a compound Pt<sub>3</sub>Ti, which facilitates crystallization of the perovskite PZT phase; without Ti, crystallization is more difficult and occurs via the growth of dendritic crystallites. Several optical and electrical properties of the PZT films have been measured; the first results indicate high dielectric constants ( $\epsilon \simeq 480$ ) and acceptable ferroelectric behaviour.



### Tin dioxide sol-gel derived thin films deposited on porous silicon

Cornel Cobianu <sup>a,\*</sup>, Cristian Savaniu <sup>a</sup>, Octavian Buiu <sup>a</sup>, Dan Dascalu <sup>a</sup>, Maria Zaharescu <sup>b</sup>, Constanta Parlog <sup>b</sup>, Albert van den Berg <sup>c</sup>, Bela Pecz <sup>d</sup>

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 d Research Institute of Technical Physics (RITP), P.O. Box 76, H-1325 Budapest, Hungary

Accepted 28 May 1997

#### Sensors and Actuators B 43 (1997) 114-120

#### EU-COPERNICUS, "PORSIS" Project

Abstract

Undoped and Sb-doped SnO<sub>2</sub> sol-gel derived thin films have been prepared for the first time from tin (IV) ethoxide precursor and SbCl<sub>3</sub> in order to be utilised for gas sensing applications where porous silicon is used as a substrate. Transparent, crack-free and adherent layers were obtained on different types of substrates (Si, SiO<sub>2</sub>/Si). The evolution of the Sn-O chemical bonds in the SnO<sub>2</sub> during film consolidation treatments was monitored by infrared spectroscopy. By energy dispersive X-ray spectroscopy performed on the cross section of the porosified silicon coupled with transmission electron microscopy, the penetration of the SnO<sub>2</sub> sol-gel derived films in the nanometric pores of the porous silicon has been experimentally proved. © 1997 Elsevier Science S.A.

### Tin dioxide sol–gel derived thin films deposited on porous silicon

C Cobianu, C Savaniu, O Buiu, D Dascalu, M Zaharescu, C Parlog, ... Sensors and Actuators B: Chemical 43 (1-3), 114-120



g. 2. XTEM image of the porous silicon after  $SnO_2$  film sol-gel position. The thickness of the PS is about 2.2  $\mu m$ .

52 1997

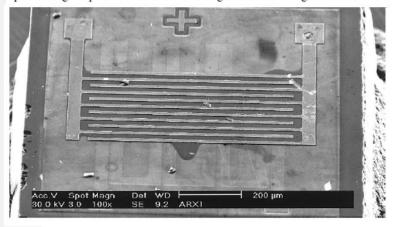
## A SnO<sub>2</sub> microsensor device for sub-ppm NO<sub>2</sub> detection

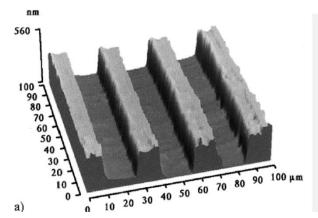
C. Cobianu a, C. Savaniu A, A. Arnautu A, R. Iorgulescu A, D. Dascalu A, G. Leo M. Mazzer B, R. Rella, P. Siciliano B, S. Capone C, L. Vasanelli C Sensors and Actuators B 58 (1999) 552–555

<sup>a</sup> National Institute of Microtechnology, PO Box 38–160, 72225 Bucharest, Romania <sup>b</sup> IME-CNR, Materiali per l'Elettronica, Campus Universitario, Via Arnesano, 73100 Lecce, Italy

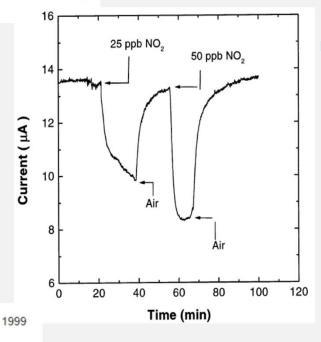
c INFM, Università di Lecce, Via Arnesano, 73100 Lecce, Italy

Gas sensors based on SnO<sub>2</sub> films deposited by sol-gel on a Si substrate have been fabricated, characterised and tested. The results of structural characterisation and the sensing tests have shown the validity of this technological approach, which is a very promising step towards the full integration of the gas sensors in VLSI Si technology. © 1999 Elsevier Science S.A. All rights









Forum Romanians in Micro- and Nanoelectronics, 6 November 2018, Romanian Academy, Bucharest, Romania

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## SnO<sub>2</sub> sol-gel derived thin films for integrated gas sensors

Sensors and Actuators B 77 (2001) 496-502

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Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, P.O. Box 6100, FIN-02015, Espoo, Finland In this paper, we present for the first time the compatibility of sol-gel method for SnO<sub>2</sub> thin film preparation with the silicon technology or integrated gas sensor microfabrication. An integrated circuit (IC) compatible test structure of medium power consumption equipped with boron-doped silicon heater and Au/W metallization is developed. The acid composition of the (liquid) sol phase, the thermal budget of ensing layer structuring, selective wet etching of SnO<sub>2</sub> sensing film, thickness uniformity and step coverage of SnO<sub>2</sub> sol-gel films are fitted with the requirement of above test structure where metal layer is deposited before SnO2 film. Nanometric grain sizes of undoped and intimony doped polycrystalline SnO<sub>2</sub> films are obtained, as revealed by XRD investigations. The AFM measurements of SnO<sub>2</sub> thin films leposited on existing Au/W metallization shown the excellent step coverage and morphology of SnO2 films used for gas sensing pplications. Low temperature gas sensing properties of our SnO<sub>2</sub> sol-gel derived thin films in reducing (CH<sub>4</sub>, CH<sub>3</sub>COOH) and oxidizing NO<sub>2</sub>) are preliminary reported by using our integrated test structure. © 2001 Elsevier Science B.V. All rights reserved.

SnO2 sol-gel derived thin films for integrated gas sensors

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C Cobianu, C Savaniu, P Siciliano, S Capone, M Utriainen, L Niinisto Sensors and Actuators B: Chemical 77 (1-2), 496-502

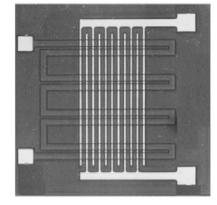
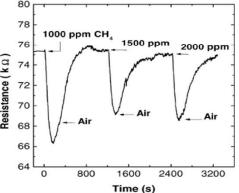
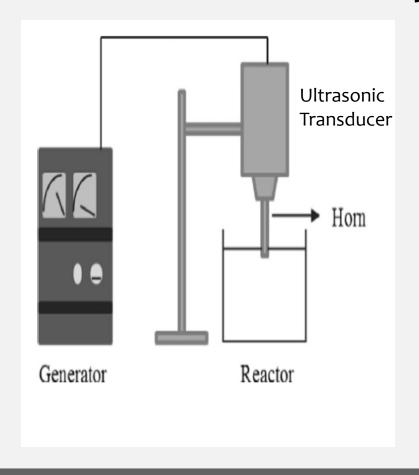


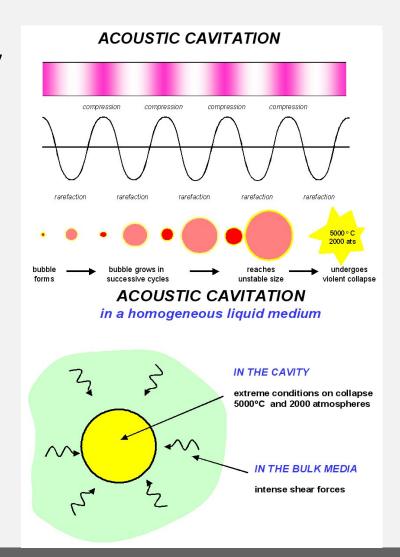
Fig. 1. Top view of the SnO2 gas sensor lay-out. Meandered heater with two W/Au contacts and W/Au sensor electrodes can be identified from this



# Functional films prepared by Sonochemistry

## Basics of sonochemistry





# (12) United States Patent Cobianu et al.

(10) Patent No.: US 9,604,191 B2

(45) **Date of Patent:** Mar. 28, 2017

#### METHOD AND SYSTEM FOR FLAMMABLE GAS DETECTION COMPRISING A SONICATED NANOSTRUCTURED METAL OXIDE

Applicant: HONEYWELL INTERNATIONAL

INC., Morristown, NJ (US)

Inventors: Cornel P. Cobianu, Bucharest (RO);

Bogdan-Catalin Serban, Bucharest

(RO); Alisa Stratulat, Bucharest (RO);

Viorel Georgel Dumitru, Prahova (RO); Mihai Brezeanu, Bucharest

(RO); Octavian Buiu, Bucharest (RO)

Assignee: Honeywell International Inc., Morris

Plains, NJ (US)

### (57) ABSTRACT

The present disclosure relates to a nanostructured palladiumbased flammable gas detector synthesized using sonochemistry. The nanostructured palladium-based flammable gas detectors may use nanostructured sensing materials to allow reduction of power consumption, where the nanostructures reduce power consumption due to their large specific area and increased porosity. The nanostructures may increase the number of active sensing sites, allowing the surface energy to be high enough for sensing reactions to occur without requiring significant external thermal energy,

# Low Power Resistive Oxygen Sensor Based on Sonochemical SrTi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>2.8</sub> (STFO40) Alisa Stratulat <sup>1</sup>, Bogdan-Catalin Serban <sup>1,\*</sup>, Andrea de Luca <sup>2</sup>, Viorel Avramescu <sup>1</sup>,

Alisa Stratulat <sup>1</sup>, Bogdan-Catalin Serban <sup>1,\*</sup>, Andrea de Luca <sup>2</sup>, Viorel Avramescu <sup>1</sup>, Cornel Cobianu <sup>1</sup>, Mihai Brezeanu <sup>1</sup>, Octavian Buiu <sup>1</sup>, Lucian Diamandescu <sup>3</sup>, Marcel Feder <sup>3</sup> Syed Zeeshan Ali <sup>4</sup> and Florin Udrea <sup>2,4</sup>

Sensors 2015, 15, 17495-17506; doi:10.3390/s150717495

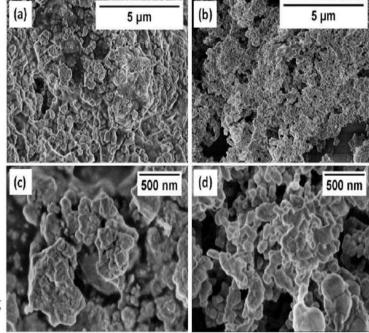
- Honeywell Romania SRL, Sensors and Wireless Laboratory Bucharest (SWLB), Bucharest 020339, Romania; E-Mails: alisa.stratulat@honeywell.com (A.S.); viorel.avramescu@honeywell.com (V.A.); cornel.cobianu@honeywell.com (C.C.); mihai.brezeanu@honeywell.com (M.B.); octavian.buiu@honeywell.com (O.B.)
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- National Institute of Materials Physics, Bucharest-Magurele, P.O. Box. MG-7, Magurele 77125, Romania; E-Mails: diamand@infim.ro (L.D.); mfeder@infim.ro (M.F.)
- <sup>4</sup> Cambridge CMOS Sensors Ltd., Cambridge CB4 0DL, UK; E-Mail: zeeshan.ali@ccmoss.com

EU-FP-7 "SOI-HITS" project, rewarded for technology innovation on entire FP-7 program, in December 2015 at Berlin

# Low Power Resistive Oxygen Sensor Based on Sonochemical SrTi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>2.8</sub> (STFO40)

Alisa Stratulat <sup>1</sup>, Bogdan-Catalin Serban <sup>1</sup>,\*, Andrea de Luca <sup>2</sup>, Viorel Avramescu <sup>1</sup>, Cornel Cobianu <sup>1</sup>, Mihai Brezeanu <sup>1</sup>, Octavian Buiu <sup>1</sup>, Lucian Diamandescu <sup>3</sup>, Marcel Feder <sup>3</sup> Syed Zeeshan Ali <sup>4</sup> and Florin Udrea <sup>2,4</sup>

Abstract: The current paper reports on a sonochemical synthesis method for manufacturing nanostructured (typical grain size of 50 nm) SrTi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>2.8</sub> (Sono-STFO40) powder. This powder is characterized using X ray-diffraction (XRD), Mössbauer spectroscopy and Scanning Electron Microscopy (SEM), and results are compared with commercially available SrTi<sub>0.4</sub>Fe<sub>0.6</sub>O<sub>2.8</sub> (STFO60) powder. In order to manufacture resistive oxygen sensors, both Sono-STFO40 and STFO60 are deposited, by dip-pen nanolithography (DPN) method, on an SOI (Silicon-on-Insulator) micro-hotplate, employing a tungsten heater embedded within a dielectric membrane. Oxygen detection tests are performed in both dry (RH = 0%) and humid (RH = 60%) nitrogen atmosphere, varying oxygen concentrations between 1% and 16% (v/v), at a constant heater temperature of 650 °C. The oxygen sensor, based on the Sono-STFO40 sensing layer, shows good sensitivity, low power consumption (80 mW), and short response time (25 s). These performance are comparable to those exhibited by state-of-the-art O<sub>2</sub> sensors based on STFO60, thus proving Sono-STFO40 to be a material suitable for oxygen detection in harsh environments.

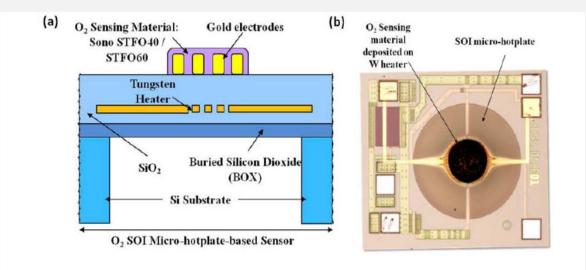


**Figure 5.** SEM micrographs of (a) commercial STFO60 (10 kX); (b) Sono-STFO40 (10 kX); (c) commercial STFO60 (50 kX); (d) Sono-STFO40 (50 kX).

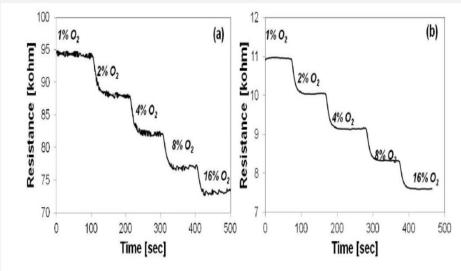
# Low Power Resistive Oxygen Sensor Based on Sonochemical SrTi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>2.8</sub> (STFO40)

Alisa Stratulat <sup>1</sup>, Bogdan-Catalin Serban <sup>1,\*</sup>, Andrea de Luca <sup>2</sup>, Viorel Avramescu <sup>1</sup>, Cornel Cobianu <sup>1</sup>, Mihai Brezeanu <sup>1</sup>, Octavian Buiu <sup>1</sup>, Lucian Diamandescu <sup>3</sup>, Marcel Feder <sup>3</sup> Syed Zeeshan Ali <sup>4</sup> and Florin Udrea <sup>2,4</sup>

Sensors 2015, 15, 17495-17506; doi:10.3390/s150717495



**Figure 1.** (a) O<sub>2</sub> resistive sensor structure employing a CMOS-compatible SOI micro-hotplate as substrate and Sono-STFO40 as sensing layer; (b) Top-view of the manufactured O<sub>2</sub> resistive sensor.



**Figure 6.** Oxygen sensor response in dry nitrogen atmosphere (1%–16% O<sub>2</sub>) for: (a) Sono-STFO40 and (b) STFO60.

Forum Romanians in Micro- and Nanoelectronics, 6 November 2018, Romanian Academy, Bucharest, Romania



### (19) United States

# (12) Patent Application Publication (10) Pub. No.: US 2017/0328855 A1

Cobianu et al.

FET BASED HUMIDITY SENSOR WITH BARRIER LAYER PROTECTING GATE DIELECTRIC

Applicant: Honeywell International Inc., Morris

Plains, NJ (US)

Inventors: Cornel Cobianu, Bucharest (RO);

Alisa Stratulat, Bucharest (RO); Bogdan Serban, Bucharest (RO);

Octavian Buiu, Bucharest (RO); Cazimir Gabriel Bostan, Bucharest

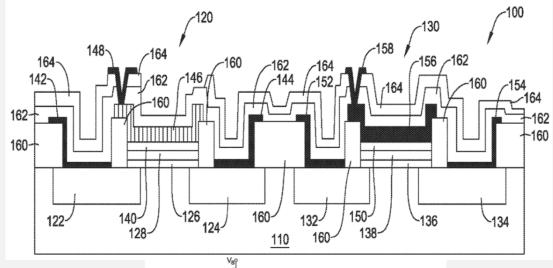
(RO); Mihai Brezeanu, Bucharest

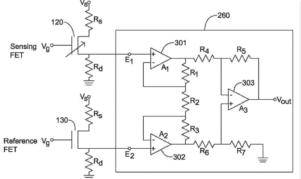
(RO); Stefan Dan Costea, Bucharest

(RO); Richard Davis, Plano, TX (US)

(43) **Pub. Date:** 

Nov. 16, 2017





### **Quartz – MEMS Technology: Differential Pressure and Temperature Sensors**

# (12) United States Patent Cobianu et al.

(10) Patent No.:

US 7,243,547 B2

(45) Date of Patent:

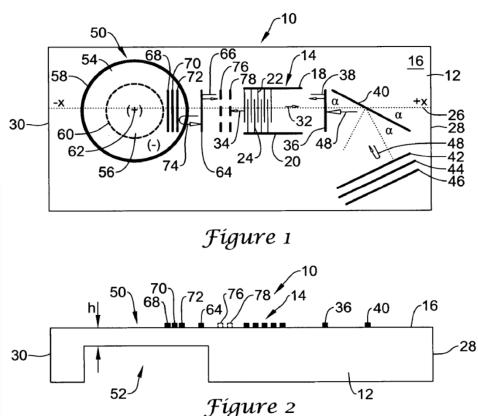
Jul. 17, 2007

- (54) MEMS SAW SENSOR
- (75) Inventors: Cornel P. Cobianu, Bucharest (RO);

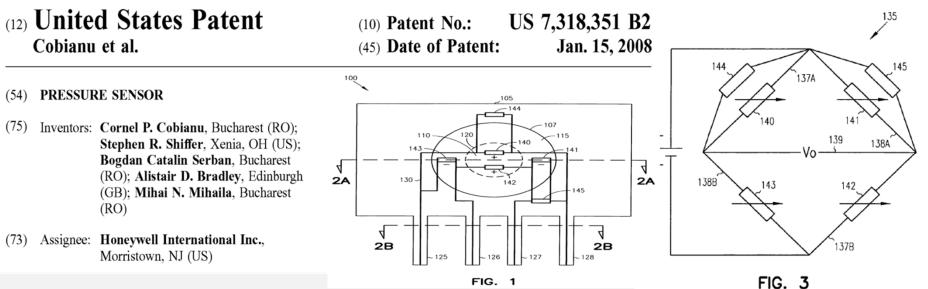
  Ioan Pavelescu, Bucharest (RO);

  James D. Cook, Freeport, IL (US)
- (73) Assignee: **Honeywell International Inc.**, Morristown, NJ (US)

Devices and methods for acoustically measuring temperature and pressure are disclosed. An illustrative SAW sensor can include an electrode structure that transmits and receives surface acoustic waves along a SAW delay line, a temperature sensor for measuring temperature along a first direction of the SAW delay line, and a pressure sensor for measuring pressure along a second direction of the SAW delay line. The SAW sensor can include an antenna that wirelessly transmits and receives RF signals to and from an electrical interrogator unit that can be used to power the SAW sensor.



## Low cost differential pressure sensor on plastic package



A pressure sensor is constructed of a plastic package. The plastic package incorporates in the same material a sensing diaphragm including tensile and compression regions. Deposited on the diaphragm are metal electrodes and a polymer film having piezoresistive properties. The electrodes and/or the polymer film are directly printed onto the plastic package without the use of a mask.

## Lead-free Electrochemical O<sub>2</sub> sensors

(12) United States Patent Cobianu et al.

(10) Patent No.:

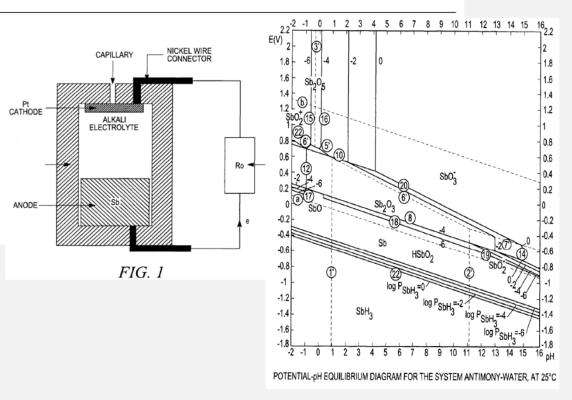
US 9,557,289 B2

(45) **Date of Patent:** Jan. 31, 2017

- (54) LEAD-FREE ELECTROCHEMICAL GALVANIC OXYGEN SENSOR
- (75) Inventors: Cornel Cobianu, Bucharest (RO);

  Bogdan-Catalin Serban, Bucharest
  (RO); Bryan Stewart Hobbs, West
  Sussex (GB)
- (73) Assignee: Life Safety Distribution AG, Hegnau (CH)
- (57) ABSTRACT

A lead-free, self-corrosion-free electrochemical galvanic oxygen sensor is provided. The preferred sensor includes a container, the container including a lead-free anode, an alkali electrolyte, a carbon platinized with platinum cathode and a nickel wire current collector, wherein the container further includes a diffusion barrier that causes the sensor to operate in the limiting current region.



### (12) United States Patent

#### Cobianu et al.

## THREADED COUPLING DEVICE WITH NOZZLE FOR GWR MEASUREMENTS IN NON-METALLIC TANKS

(72) Inventors: Cornel Cobianu, Bucharest (RO); Ion

Georgescu, Bucharest (RO); Stuart James Heath, Surrey (CA); Michael Kon Yew Hughes, Vancouver (CA);

Frank Martin Haran, North

Vancouver (CA)

(73) Assignee: Honeywell International Inc.,

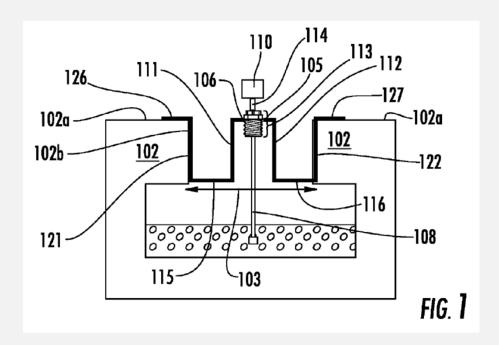
Morristown, NJ (US)

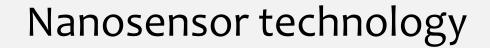
(57) ABSTRACT

A coupling device for coupling a threaded feed-through of a process connection to provide a launcher for a non-metallic storage tank. The storage tank includes a tank aperture in its top surface. The coupling device includes a foil nozzle including an inner upper metal foil surface that includes a threaded aperture for securing the feed-through thereto, and a first and second lower metal foil surface on respective sides of the upper metal foil surface. The foil nozzle also includes a first and a second foil level transition region disposed between the respective sides of the inner upper metal foil surface and the first and second lower metal foil surface. The foil nozzle can be configured in a cylindrical, horn, or a corrugated horn shape.

(10) Patent No.: US 9,518,856 B2

(45) **Date of Patent:** Dec. 13, 2016





# United States Patent Cobianu

(10) Patent No.:

(45) **Date of Patent:** 

US 8,980,666 B2 Mar. 17, 2015

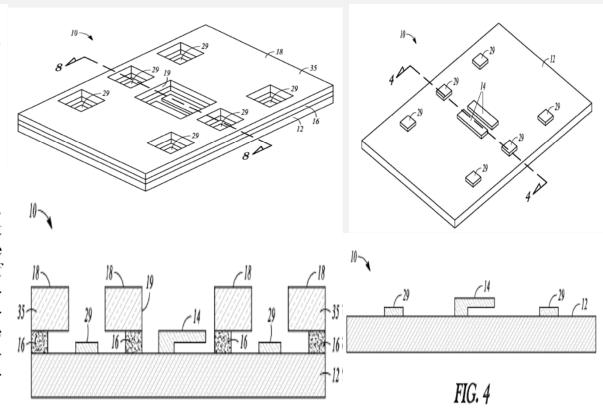
#### METHOD OF FABRICATING SENSORS HAVING FUNCTIONALIZED RESONATING BEAMS

Inventor: Cornel P. Cobianu, Bucharest (RO)

Assignee: Honeywell Romania s.r.l. (RO)

(57) ABSTRACT

Some embodiments relate to method of fabricating a sensor. The method includes providing a substrate wafer that includes a suspended beam; adding an adhesive layer to the substrate wafer such that the adhesive layer covers portions of the substrate without covering the suspended beam; positioning a cover wafer onto the adhesive layer such that the suspended beam is exposed to ambient air through openings in the cover wafer; and functionalizing the suspended beam by contacting the suspended beam with materials through the opening in the cover wafer.



Research performed within EU-FP-7 NEMSIC Project, Coordinator Prof. Adrian Ionescu, EPFL

Forum Romanians in Micro- and Nanoelectronics, 6 November 2018, Romanian Academy, Bucharest, Romania

(12) United States Patent Cobianu et al.

(10) Patent No.: US 8,479,560 B2 (45) Date of Patent: Jul. 9, 2013

Electronic Block

Electronic Block

- (54) DIFFERENTIAL RESONANT SENSOR APPARATUS AND METHOD FOR DETECTING RELATIVE HUMIDITY
- (75) Inventors: Cornel Cobianu, Bucharest (RO);

Bogdan Serban, Bucharest (RO); Mihai

N. Mihaila, Bucharest (RO)

(73) Assignee: Honeywell International Inc.,

Morristown, NJ (US)

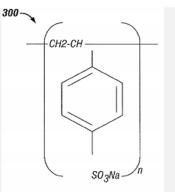
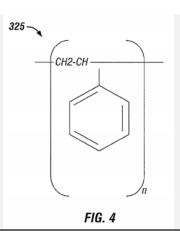


FIG. 3

Sensing layer
Sulfonated Polystyrene



135

130

145

140-

125

Reference layer Polystyrene

-170

 $f_0 = f_s - f_{ref}$ 

<sup>1</sup>ref

150

-120

Mixer

### **United States Patent**

Serban et al.

FUNCTIONALIZED MONOLAYERS FOR CARBON DIOXIDE DETECTION BY A RESONANT NANOSENSOR

Inventors: Bogdan-Catalin Serban, Bucharest

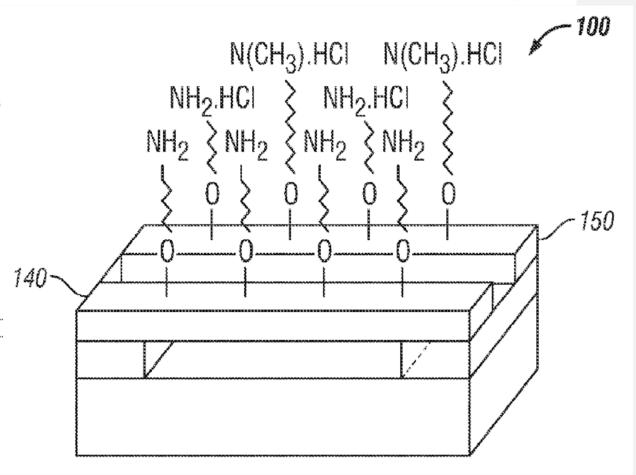
(RO); Cornel Cobianu, Bucharest (RO); Mihai N. Mihaila, Bucharest (RO); Viorel-Georgel Dumitru, Ploiesti (RO)

Assignee: Honeywell International Inc.,

Morristown, NJ (US)

A resonant nanosensor apparatus associated with a functionalized monolayer for detecting carbon dioxide and a method of forming the same. A wafer including a sensing vibrating beam and a reference vibrating beam may be functionalized with a functional group in order to form a sensing self monolayer. The sensing self assembled monolayer may be configured by bridging oxygen or carbon atoms covalently bonded with respect to the vibrating beams. A liquid solution of hydrochloric acid may then be applied to the sensing self assembled monolayer at the surface of the reference beam by a direct printing process to obtain a reference monolayer. The liquid solution of HCl transforms the functional groups responsible for the carbon dioxide detection into protonated groups, which do not react with carbon dioxide, but possess visco-elastic properties similar to that of the sensing monolayer.

(10) Patent No.: US 8,230,720 B2 (45) Date of Patent: Jul. 31, 2012



## **Conclusions**

### W. Edwards Deming:

"Learning is not compulsory... neither is survival". It is not necessary to change, survival is not compulsory
"In God we trust. All the other must bring data"

#### Einstein:

"Life is like riding a bicycle. To keep your balance you must keep moving"

"Make things as simple as possible, but not simpler"

"Imagination is more important than knowledge. For knowledge is limited, whereas imagination embraces the entire world, stimulating progress, giving birth to evolution."

