

SYMPOSIUM A
Semiconductor Materials for Sensing

November 28 - December 2, 2004

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TUTORIAL

FT A: New Approaches in Design, Synthesis, and Integration of Semiconductor Sensors Sunday November 28, 2004 1:30 PM - 5:00 PM Room 202 (Hynes)

Sensing devices (alarms and safety devices in cars, indoor and outdoor air-quality monitoring, and health monitoring) are now part of our everyday life, and the demand for sensors and actuators keeps increasing. Sensors based on semiconductors are extremely popular due to their low cost and ability to be integrated in electronic devices. However, industry still needs improvements of the sensors properties, such as smaller size, better selectivity and sensitivity, and faster response, together with high device reliability, easy integration in electronic devices, and low production costs.

This tutorial will be presented by two instructors whose work on sensors is internationally recognized.

Ted Kamins of Hewlett-Packard Laboratories will focus on semiconductor sensors that can be integrated onto silicon-integrated circuits and sensors that can be fabricated using IC-based technology. The use of new materials such as metal-catalyzed nanowires and nanotubes will be discussed, and the tradeoff between doping and physical size for field-effect devices will be considered. Different kinds of sensors detecting various analytes, such as dangerous chemical and biological species, gases, strain, and visible and other radiation will be analyzed, and the characteristics critical for practical applications will be reviewed. Johannes Schwank of the University of Michigan will review the recent advances in combinatorial materials synthesis and theoretical modeling, and simulation of gas-solid interactions based on density functional theory. A combined application of sophisticated experimental and theoretical tools aimed at design and synthesis of novel sensors might have a lasting impact on general research approaches in the chemical sensor community. The potential of this approach in the field of gas sensing will be discussed in terms of device architecture, sensing concepts, and new front-end materials.

Instructors:

Ted Kamins

Hewlett-Packard Laboratories

Johannes Schwank

University of Michigan

SESSION A1: Advanced Materials and Processing

Chairs: Marie-Isabelle Baraton and Norimitsu

Murayama

Monday Morning, November 29, 2004

Back Bay D (Sheraton)

8:30 AM *A1.1

Porous Tin Dioxide Materials for Gas Sensor Application.

Makoto Egashira¹, Yasuhiro Shimizu² and Takeo Hyodo¹, ¹Materials Science and Engineering, Nagasaki University, Nagasaki, Japan; ²Graduate School of Science and Technology, Nagasaki University, Nagasaki, Japan.

A particular focus is currently being given to nanosized or nanostructured semiconductor metal oxides as sensor materials, since grain-size reduction and gas-diffusion control have been proved to be useful for improving the sensing properties of semiconductor gas sensors. From the viewpoint of simplicity for gas diffusion control, semiconductor metal oxides with controlled porous structure in the range of nano to submicron size are of very interest. Therefore, our latest studied have been directed to improving gas sensing properties by controlling the porous structure. First example is synthesis of thermally stable mesoporous SnO₂ (m-SnO₂) powder with pores in the range of 1-10 nm by employing the self-assembly of a cationic surfactant and phosphoric acid treatment of as-precipitated products. The m-SnO₂ powder thus prepared showed sufficient thermal stability along with a sharp pore size distribution at ca. 1.6 nm, a large specific surface area of 305 m² g⁻¹ and a small crystallite size of ca. 2.0 nm even after calcination at 873 K for 5 h in air. The thick film sensors fabricated with m-SnO₂ powder showed improved H₂ sensing properties, in comparison with those observed for another SnO₂ (c-SnO₂) sensor fabricated conventionally. The second is surface modification of c-SnO₂ powder with an m-SnO₂ layer. Both H₂ and NO_x responses could be improved by the surface modification. The m-SnO₂ layer was considered to act as a diffusion control layer for gaseous O₂ in detecting H₂, but as an adsorbent for NO_x in the latter case. In addition, Ru metal loading on c-SnO₂ powder prior to the

modification with the m-SnO₂ layer resulted in larger H₂ response than the sensor prepared by the loading after the modification. The improved H₂ response was considered to arise from a synergistic effect of the diffusion control by the m-SnO₂ layer and the chemical sensitization by the Ru loaded on the SnO₂ powder. The last example is fabrication of periodic submicron-sized porous SnO₂ thick films by a colloidal crystal templating method combined with sol-gel process by employing polymethylmethacrylate (PMMA) microspheres as a template. The resulting film consisted of a self-standing framework of interconnected hollow SnO₂ microspheres. Both H₂ and NO_x responses were found to be controlled by selecting the particle size of PMMA used. In my presentation, advantages of the above three methods in improving the sensing properties are to be reviewed more in detail and then remaining problems will also be discussed.

9:00 AM A1.2

Organically Hybridized In₂O₃ Thin Film Gas Sensors.

Ichiro Matsubara, Norimitsu Murayama, Woosuck Shin and Noriya Izu; National Institute of Advanced Industrial Science & Technology, Nagoya, Japan.

Metal oxide semiconductors have been widely used for gas sensors. These materials working on the ordinal combustion mechanism detect any kinds of reducing gases in principle. The lack of gas selectivity, e.g. between CO and H₂ gases, has therefore been regarded as a problem to be solved. We have already reported that the organic-inorganic hybridization approach is one of the good ways to improve the gas selectivity. SnO₂ thin films hybridized to organic component with amino groups show anomalous resistance increasing response to CO gas, whereas they show resistance decreasing response to H₂ and CH₄ gases. The appearance of the anomalous resistance increasing response can be controlled by functional group of the organic component. In order to confirm the effectiveness of the organic-inorganic hybridization approach, here we have prepared In₂O₃ thin film gas sensors hybridized to organic components with various functional groups, and evaluated the gas sensing properties.

9:15 AM A1.3

Flame-made Nanoparticles for Gas Sensors. **Sotiris Pratsinis¹,** Lutz Madler¹, Thorsten Sahn², Alexander Gurlo², Nicolai Barsan² and Udo Weimar²; ¹Particle Technology Laboratory, Mechanical & Process Engineering, ETH Zurich, Zurich, Switzerland; ²Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen, Germany.

Metal oxides in general and SnO₂, in particular, have attracted the attention of many users and scientists interested in gas sensing under atmospheric conditions. SnO₂ sensors are the best-understood prototypes of oxide-based gas sensors [1]. The performance of metal oxide gas sensors is strongly related to the properties of the ceramic such as grain size, morphology, surface groups, etc. It has been shown that flame spray pyrolysis (FSP) enables the controlled synthesis of such materials and bears the advantage of complete manufacture of nanopowder in a single high temperature process step leading to controlled microstructure and noble metal loadings if desired [2]. Here, single crystalline tin oxide particles of 17 nm in size were produced using the versatile FSP technique. The particles were only slightly aggregated and were directly used for thick film sensor deposition by drop coating. When exposing the sensor to oxidizing gases (such as NO₂) its resistance increases, while reducing gases (propanal and CO) decreases the resistance of the sensor. This behavior is typical for the tin dioxide which is an n-type semiconductor. The fabricated sensors show low output signals to CO even at high concentrations (> 500 ppm, both in humid and dry air) and much higher signals with propanal present, which corresponds to a typical behavior for the undoped SnO₂. At low operating temperatures (<300 C), the sensor signals to propanal and CO are higher in dry air in comparison with the humid one. Compared to state of the art SnO₂ thick film sensors, the signal response to NO₂ and propanal of the reported sensors was significantly faster and showed the expected power law behavior. Flame-made SnO₂ nanoparticles showed high and fast response to both reducing (propanal) and oxidizing (NO₂) gases. In-situ flame deposition of Pt and Pd on SnO₂ particles, which is known to be a good method for promoting the detection of CO, is the next step towards a new generation of tailor-made sensors from gas phase derived fine powders. [1] N. Barsan, U. Weimar, J. Phys. Condens. Matter 15, R813-R839 (2003). [2] L. Madler, W. J. Stark, S. E. Pratsinis, J. Mater. Res. 18, 115-120 (2003). [3] T. Sahn, L. Madler, A. Gurlo, N. Barsan, S.E. Pratsinis, U. Weimar, Sensors and Actuators B-Chemical, 98 (2-3) 148-153 (2004).

9:30 AM *A1.4

Nano-Design of Oxide Particles and Electrode Structure for High Sensitivity NO₂ Sensor Using WO₃ Thick Film.

Jun Tamaki, Department of Applied Chemistry, Ritsumeikan University, Kusatsu-shi, Shiga, Japan.

Novel sensor design for high sensitivity gas sensors has been investigated for the detection of dilute NO₂ using WO₃ thick film. First, concerning nano-design of oxide particles, the disk-shaped WO₃ particles were prepared by dehydration of H₂WO₄ obtained in wet process. The particle size was 300 nm in diameter and 20 nm in thickness when the powder was calcined at 400 °C for 3 h. Such disk-shaped WO₃ particles were deposited on Au comb-type microelectrode (line width : 5 μm, distance between lines : 5 μm) to be WO₃ thick film sensor. The thick film consisted of dense packing of disk-shaped particles and the sensor showed the excellent sensing properties to dilute NO₂ at optimized thickness (7 μm). The sensitivity ($S=R_g/R_a$) to 0.05 ppm NO₂ was as high as 45 with fast response-recovery characteristics, where R_a and R_g were resistance in air and in NO₂ containing air, respectively. Further, it was demonstrated that the WO₃ thick film sensor could be used for environmental NO₂ monitoring. Second, in order to investigate the effect of microelectrode, the nano-gap electrode with various gap sizes (330-1500 nm) was designed by means of MEMS techniques (photolithography and FIB techniques). In this case, the line width was set to 11-15 μm. The WO₃ thin film was deposited on nano-gap to be nano-gas-sensor. When the gap size was decreased less than 800 nm, the sensitivity to dilute NO₂ tended to increase with decreasing gap size. The sensitivity to 0.5 ppm NO₂ was as high as 47 for nanosensor with 330 nm gap. The sensor resistance is the sum of interface resistance between WO₃ particle and electrode and grain boundary resistance. The number of WO₃ particle in nano-gap is decreased with decreasing gap size, suggesting the contribution of interface resistance to total sensor resistance is increased. If the resistance change at interface is much larger than that at grain boundary, the sensitivity is increased with decreasing gap size. From the result of simple calculation, it was found that the resistance change at interface was 13-50 times larger than that at grain boundary. Further, it is expected that the sensitivity exceeds 100 when the 50 nm gap is realized. As mentioned above, the designs of not only nano-particles but also of nano-electrode are important for the fabrication of high sensitivity gas sensor.

10:30 AM A1.5

Near-Surface Characteristics of Highly Sensitive Metal Oxide Thin Films. George Kiriakidis^{1,2}, Nikos Katsarakis^{1,3} and Michalis Katharakis^{1,3}; ¹IESL, FORTH, Heraklion, Crete, Greece; ²Physics, University of Crete, Crete, Greece; ³MSLG, School of Applied Technology, Technological Educational Institute, Crete, Greece.

We report on the structural (XRD, AFM, SEM), optical (UV-VIS, FT-IR), electrical and sensing properties of dc sputtered InOx and ZnOx thin films. They both show resistivity changes of five to eight orders of magnitude at room temperature after exposure to UV light and subsequent Ozone or NO₂ treatment. Such behaviour underlines the potential of utilizing these films as low temperature gas sensing elements. Particular interest was paid on the properties and characteristics of the top few layers that are actively involved in the oxidation and photoreduction processes. Characterization of InOx coatings on silicon substrates by EPMA and SIMS has shown a homogeneous structure in depths up to 150nm with an average In/O atomic ratio of 0.68, thus slightly off stoichiometric (In₂O_{2.94}). However, near-surface region (0-20nm) depth profile analysis has revealed a noticeable deficit in oxygen presence in the top 5nm for films in the "conducting" state, after UV exposure. The In/O atomic ratio concentration ($C_{In}[at\%] / C_{O}[at\%]$) at the surface as derived by SIMS-depth profiles ranged from 0.73 to 0.62. These results were confirmed by parallel experiments of in-situ near-surface gas analysis utilizing Quadrupole Mass Spectrometry during UV exposure showing a clear correlation of oxygen out-diffusion process with the transition from "insulating" to "conducting" state and are in line with earlier conductometric experiments. Analyses on the sensing response for alumina-based transducers of InOx films with a thickness in the range of 20-200nm studied in the 50-300 °C temperature range have shown maximum sensitivity ($S=R_{gas}/R_{air}$) for the thinner samples (<50nm) operating at around 100 °C. The minimum detection levels at 40% RH were in the range of 10 and 50 ppb for O₃ and NO₂ respectively. On-going experiments on Sound Acoustic Wave (SAW) devices based on dc sputtered InOx and ZnOx thin films fabricated on LiNbO₃ substrates indicate the capability of achieving sensing levels in the sub-ppb range.

11:00 AM A1.6

Room Temperature Hydrogen Gas Sensitivity of Nanocrystalline Doped-Tin Oxide Sensor Incorporated into MEMS Device. Satyajit V. Shukla¹, Lawrence Ludwig², Hyoung Cho¹ and Sudipta Seal¹; ¹Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida; ²Kennedy Space Center (KSC-NASA), Kennedy Space Center, Florida.

Nanocrystalline indium oxide (In₂O₃) doped-tin oxide (SnO₂) thin film is sol-gel dip-coated on the microelectromechanical-systems

(MEMS) devices as a room temperature hydrogen sensor. The effect of ultraviolet (UV) radiation on the room temperature hydrogen gas sensitivity ($S=R_{air}/R_{gas}$, where R_{air} is the sensor resistance in air and R_{gas} is that in the presence of reducing gas) of the present sensor is systematically studied. It is shown that the exposure to the UV-radiation results in the deterioration of the hydrogen gas sensitivity of the present sensor, which is in contrast with the earlier reports. Very high hydrogen gas sensitivity as high as 110000 is observed, for 900 ppm hydrogen, without exposing the sensor to the UV-radiation. In the presence of UV-radiation, however, the hydrogen gas sensitivity reduces to 200. The drastic reduction in the hydrogen gas sensitivity due to the UV-exposure is explained on the basis of the constitutive equation for the gas sensitivity of nanocrystalline semiconducting oxides thin film sensor. Novel techniques for enhancing further the room temperature hydrogen gas sensitivity and selectivity of the present sensor are highlighted.

11:15 AM A1.7

Selective, Sensitive, and Tunable Nanostructure Modified Porous Silicon Gas Sensor. James L. Gole¹, Peter J. Hesketh¹, Stephen Lewis¹ and John De Bohr¹; ¹School of Physics, Georgia Institute of Technology, Atlanta, Georgia; ²School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia.

A porous silicon interface is transformed within the framework of nanotechnology to develop highly efficient sensors¹, interactive support surfaces and nanophotocatalytic frameworks. We extend the concept of a rapid, reversible, and sensitive porous silicon (PS) gas sensor, based upon a uniquely formed highly efficient electrical contact to a nanopore covered microporous array, to introduce selectivity and to develop a novel fast Fourier transform technique which allows sensing in the presence of a drifting baseline. Utilizing a combination of photoluminescence induced electroless metallization and electron beam deposition as a means to obtaining a highly efficient electrical contact we subsequently demonstrate the detection of HCl, NH₃, CO and NO at the ppm (calibrated) and ppb level. The problem of spreading resistance (200k W-MW) is overcome as low resistance contacts which can approach 20W are made to the PS structure^{1,4}. The response of the device, which can operate with limited selectivity, at a bias voltage of 1-10 mV, is rapid and reversible. With an electroless gold treatment, introducing gold nanostructures to the PS framework, we find that the impedance response of the device to ammonia increases by 2.5 times, while the CO and NO responses are virtually unchanged. With an electroless tin coating, to produce a nanoscale tin oxide structure, the room temperature responses to NH₃, NO, and CO are all amplified. With this combination, we introduce a significant degree of selectivity. By introducing an FFT analysis to the rapidly reversible, linearly responding, PS gas sensor, the gas response can now be acquired and filtered on a drifting baseline, further increasing sensitivity. These sensors should be compared with porous silicon based sensors with resistances in excess of 200kΩ and a 2V bias voltage, SnO₂ sensors operating at 300-500°C, and other similar gas sensors operating at 2-5V. The sensor suites are now being extended using nanoscale titania based quantum dot (QD) photocatalysts will be placed within the pores of PS and excited using PS electrochromism or photoluminescence to excite visible light absorbing QDs. Using a nanoscale exclusive synthesis route, in seconds, at room temperature, we produce nitrogen doped, stable, and environmentally benign TiO_{2-x}N_x photocatalysts whose optical response, now not limited to the ultraviolet, can be tuned across the visible region. This synthesis, which can be simultaneously accompanied by metal atom seeding, is accomplished through the direct nitration of anatase TiO₂ nanostructures with alkyl ammonium salts. Tunability throughout the visible depends on the degree of nanoparticle agglomeration and the influence of metal seeding. These photocatalysts can be transformed from liquids to gels and placed on the surface of a sensor to produce a significantly improved photocatalytically induced solar pumped sensor response.

11:30 AM A1.8

Hybrid Enzyme Based Porous Silicon Platform for Chemical Warfare Agent Detection. Sonia E. Letant², Bradley R. Hart¹, Staci R. Kane³, Masood K. Hadi⁴, Sharon J. Shields¹, Tu-Chen Cheng⁵, Vipin K. Rastogi⁵ and John G. Reynolds¹; ¹Forensic Science Center, Lawrence Livermore National Laboratory, Livermore, California; ²Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California; ³Environmental Restoration Division, Lawrence Livermore National Laboratory, Livermore, California; ⁴Lockheed Martin Corporation, Sandia National Laboratory, Livermore, California; ⁵US Army Edgewood Chemical and Biological Center, Aberdeen Proving Ground, Aberdeen, Maryland.

A new synthetic route to covalently anchor bio-molecules to photoluminescent porous silicon while preserving the optical properties of the material has been developed. The hydride terminated porous silicon surface was covalently functionalized with

t-butyloxycarbonyl protected amine using a photochemical process that provides reactive functionality for further attachment. Protein cross-linker chemistry is then used to extend the linker and immobilize various molecules such as antibodies, proteins and enzymes. In a first step, streptavidin was chosen to demonstrate the effectiveness of the ligand system for bio-molecule attachment and FTIR spectroscopy, Mass Spectrometry and luminescence characterization demonstrated covalent functionalization as well as strong luminescence retention. The glucuronidase enzyme/p-nitro-phenyl-beta-glucuronide substrate test system was selected to provide a proof of concept for an enzyme-based porous silicon detector. The organophosphorous hydrolyase enzyme, OPAA was attached and tested on p-nitrophenyl-soman, a surrogate substrate for soman. The production of the hydrolysis product, p-nitrophenol, concurrently with reversible quenching of the porous silicon photoluminescence indicates, with the appropriate enzyme, this system can be used as an enzyme based detection system. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

11:45 AM **A1.9**

Sol-gel derived porous silica as a constituent material for designing optical fiber chemical sensors. Shiquan Tao, Joseph C. Fanguy, Lina Xu and Hu Xuemei; Diagnostic Instrumentation and Analysis Laboratory, Mississippi State University, Starkville, Mississippi.

Sol-gel process was used to prepare nano porous silica material. The obtained porous sol-gel silica (PSGS) has been used as a constituent material in designing optical fiber chemical sensors. A PSGS membrane coated on the surface of an optical fiber was used as a transducer for sensing moisture in air gas. A pH indicator, bromocresol purple, doped PSGS coating on an optical fiber has been used to sense ammonia in air and in water. Both of the coating based sensors are reversible and fast response. Water content in air gas down to sub-ppm level can be detected with the PSGS coated fiber optic sensor. The pH indicator doped PSGS coating based ammonia sensor can be used to sense ammonia in air and water down to ppb level. PSGS has also been used as a constituent material in preparing porous optical fiber. The obtained porous optical fiber has been used to design optical fiber chemical sensors for sensing moisture, ammonia and volatile organic compounds. A copper ions doped PSGS fiber has been tested for sensing ammonia in a high temperature gas environment. Ammonia in a high temperature air gas diffuses into the PSGS fiber, reversibly reacts with copper ions doped in the PSGS fiber to form a complex. The formed complex was detected with fiber optic spectrometric method. This sensor can detect ammonia in an air gas stream of 450 C down 0.3 ppm. Techniques of preparing PSGS, coating PSGS on an optical fiber, making porous optical fiber with PSGS as a constituent material will be discussed. Examples of optical fiber sensors using PSGS coatings and PSGS fibers as transducers for gas sensing will be presented.

SESSION A2: Nanotubes and Nanowires
Chairs: Clyde Parrish and Sudipta Seal
Monday Afternoon, November 29, 2004
Back Bay D (Sheraton)

1:30 PM ***A2.1**

Metal-Catalyzed Nanowires for Sensors. T. I. Kamins, Quantum Science Research, Hewlett-Packard Laboratories, Palo Alto, California.

As the computational power of integrated circuits increases, the need to provide input to the ICs becomes limiting and forming small sensors that can potentially be integrated with silicon ICs becomes more critical. Sensors can detect optical images, pressure or stress, and chemical or biological species, among other inputs, and can provide the signal directly to the computational portion of an IC chip. They are especially valuable if the sensors are physically small and formed by processes compatible with conventional silicon IC technology so that they can be integrated with the computational elements. This integration reduces cost and physical size; the reduced noise allows detecting weaker signals. This talk will focus on semiconductor nanowire sensors that use field effects induced by charged species near the surface of the nanowire. Metal-catalyzed nanowires will be emphasized. The formation of these nanowires will be described, along with a method of growing the nanowires between electrodes pre-formed using conventional IC technology. This technique avoids the difficulty of manipulating the nanowires to position them and to add contacts after they are grown. It allows forming a massively parallel array of nanowires to increase the surface-to-volume ratio without manipulating individual nanowires. The connections between the nanowires and the electrodes are mechanically strong and have low electrical contact resistance.

Nanowires can also be formed by other techniques, such as electron-beam lithography and nanoimprint lithography. In all cases, the physical size of the nanowire must be small so that the conductivity of the nanowire can be efficiently modulated by charged species near its surfaces. This ability to modulate the conductivity will be related to the physical size of the nanowire and the doping added to it. The sensing capability of nanowires will be briefly discussed using the example of nanowires formed by electron-beam lithography.

2:00 PM **A2.2**

Multiplexed Electrical Detection of Single Viruses. Fernando Patolsky¹, Gengfeng Zheng¹, Oliver Hayden¹, Melike Lakadamyali², Xiaowei Zhuang^{1,2} and Charles M. Lieber^{1,3}; ¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts; ²Department of Physics, Harvard University, Cambridge, Massachusetts; ³Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

We demonstrate for the first time the direct and selective electrical detection of single viruses using antibody-functionalized silicon nanowire field-effect transistors. Simultaneous electrical and optical measurements made on nanowire sensor arrays modified with antibodies against influenza A viruses show discrete conductance changes correlated directly with fluorescence signals that correspond to the binding and unbinding of single viruses at the surface of the devices. Studies of the antibody surface coverage further show that binding is selective and mediated by the antibody receptors, and moreover, can be used to investigate virus-receptor interactions. In addition, delivery of a mixture of influenza A and adenovirus to nanowires modified separately with antibodies specific for these viruses demonstrate unambiguously that different viruses can be detected in parallel on a same chip with high selectivity at the single virus level. The use of assembly methods to prepare integrated and much larger arrays of nanowire devices could enable the real-time, label-free, multiplexed electrical detection of a large number of viruses simultaneously at the single virus level, and thereby impact significantly screening for medical and biosafety applications. Lastly, these results suggest potential for electrically-based detection of single DNAs and even individual proteins.

2:15 PM **A2.3**

Single Walled Carbon Nanotube Electromechanical Sensing Materials and Devices for Structural Health Monitoring.

Jan M. Smits¹, Buzz Wincheski², JoAnne Ingram³, Neal Watkins², Min Namkung² and Phillip Williams⁴; ¹Lockheed Martin Space Operations, Hampton, Virginia; ²NASA Langley Research Center, Hampton, Virginia; ³Swales Aerospace, Hampton, Virginia; ⁴National Research Council, Hampton, Virginia.

Incorporating the use of electric field alignment and various lithography techniques, a series of single wall carbon nanotube (SWCNT) devices have been developed for use in structural health monitoring applications. The ability to alter the transport properties of SWCNT materials and devices by applying mechanical strain is demonstrated by direct displacement of nanotubes using an atomic force microscope manipulation, uniaxial loading via flexible polyimide device architecture and tensile testing of SWCNT composite materials. Test results in all cases indicate a direct correlation between increased resistance and nanotube strain. Theoretical dielectrophoretic force calculations showing nanotube alignment and deposition characteristics for sensor fabrication and FTIR / Raman analysis of aligned nanotubes are also presented.

2:30 PM **A2.4**

Quasi 1-D metal oxide chemical sensors: Fundamental and practical aspects of operation. Andrei Kolmakov¹, Sergei Kalinin², Yigal Lilach¹, Youxiang Zhang¹ and Martin Moskovits¹;

¹Department of Chemistry & Biochemistry, UCSB, Santa Barbara, California; ²Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

We manufactured and tested the performance of conductometric and field effect transistor (FET) gas sensors with an active element made of individual metal oxide nanowires and nanobelts. To elucidate the role of reduced dimensionality, defects, crystallinity, the nature of surface active sites on the sensitivity and selectivity of these sensors the comparative high vacuum versus high pressure study was undertaken using broad array of microscopy and spectroscopy techniques including TEM, SEM, XRD, TPD, Raman, Impedance and other measurements. We showed that when nanowire radius (or nanobelt's thickness) is comparable with its Debye length, the adsorption/desorption of donor/acceptor molecules on the surface of the nanowire (nanobelts) drastically alters the bulk electron density inside the nanowire manifesting superior performance of nanostructure as a chemical sensor. When nanostructure configured as a FET the availability of free electrons in the bulk for redox surface reactions can be controlled by the gate thus reactivity (sensitivity)

and selectivity of the nanowire surface can be tuned electronically. In vivo conductometric measurements on individual nanowire during its surface doping with catalytic particles manifest the drastic enhancement of the sensitivity and of this sensor due to selective adsorption and spillover effect. To address local transport behavior in the nanostructure sensor, ac and dc potential distributions in an operating device were measured using Scanning Impedance Microscopy (SIM) and Scanning Surface Potential Microscopy (SPPM) correspondingly. SSPM images reveals the importance of the local electroactive elements in the nanostructure and field-induced mobile charges on gate oxide layer, which under realistic conditions determine the sensitivity, stability and response time of the sensor.

2:45 PM **A2.5**

Ethanol-Sensing Characteristics of Tungsten Oxide Nanorod Films at Ambient Temperature. Yong Shin Kim¹, Kwangyeol Lee², Sung-Yool Choi¹, Seung-Chul Ha¹, Yoonseok Yang¹ and Youn Tae Kim¹; ¹Electronics and Telecommunication Research Institute, Daejeon, South Korea; ²Department of Chemistry, Korea University, Seoul, South Korea.

Conductometric metal-oxide-semiconductor (MOS) gas sensors are readily available commercially. They have been widely used in environmental monitoring, chemical processing controlling and personal safety, due to their high sensitivity, small dimensions, low cost and good compatibility with microelectronic processing. However, the high operation temperature of 200 - 500°C in the conventional MOS devices has been an obstacle to the development of intelligent sensing chip for small stand-alone system or wireless sensor networking applications, necessary for the requirement of low power consumption. In this presentation, we are going to introduce ethanol-sensing characteristics of the tungsten oxide films fabricated by using one-dimensional W₁₈O₄₉ nanorods, particularly at ambient temperature. Tungsten oxide nanorods were prepared by the solvothermal synthesis and were characterized as highly crystalline nanostructure with the average diameter of 4 nm, the average length of 75 nm, and the predominant growth of <010> direction, as previously reported (J. Am. Chem. Soc. **125** (2003) 3409). The sensing layers were fabricated by simply drop-coating of the nanorod solutions dispersed in isopropyl alcohol and by subsequent vacuum-drying at 100°C. Consequent films could be considered simply as collective aggregates of W₁₈O₄₉ nanorods by the aid of SEM and XRD analyses, although small amount of carbon impurities were observed in XPS spectrum. The sensing response of our nanorod tungsten oxide shows the conductivity increase upon exposure to ethanol vapor at operation temperature large than 100°C, which can be understood from the reaction mechanism of intrinsically n-type semiconductors, i.e., the increase in carrier concentration by the surface-chemical reactions between reducible molecules and MOS. However, at the temperature less than 100°C, the response shows the decrease of conductivity by the ethanol exposure. Even though this abnormal response is hard to explain clearly, it is reasonable to be attributed to the intrinsically small grain size and high surface-to-volume ratios associated with the highly crystalline nanostructures. The fabricated sensors exhibited high sensitivity with the signal-to-noise ratio of 300 for 3.5 ppm ethanol exposure, reversible response with the recovery time of 40 min, and the logarithmically response build-up with increasing ethanol concentration, log(response)∝[concentration], at ambient temperature. In addition, similar sensing characteristics were observed for other reducible-vapor detection such as ammonia, toluene, n-heptane, and acetone.

3:30 PM ***A2.6**

Sensing Properties of CNT Hybrid MOS-based Sensors. Hong-Ming Lin¹, Wei-Jen Wei-Jen Liou¹, Ching-Hong Yang¹, Tsung-Yeh Yang¹, Kuang-Nan Lin¹ and Chung-Yi Wu²; ¹Materials Engineering, Tatung University, Taipei, Taiwan; ²R&D Center, Chunghwa Picture Tubes, Taoyuan, Taiwan.

In recent years, carbon nanotubes have become intriguing materials, and have been studied in many fields of their unique properties such as high ratio of length to diameter, super strength, nano-scale structure, hydrogen storage, property of semiconductor and unknowable fields. The elaboration of an inorganic matrix containing embedded carbon nanotubes leads to a new nanocomposite. The possible applications of the CNTs nanocomposites are the intrinsic mechanical or electrical properties and gas sensing etc. The carbon nanotubes provide the large surface area that can enhance the adsorption properties of gases and the conductivity at the lower temperature for gas sensing. The gas sensing properties of the hybrid CNTs/TiO₂ and CNTs/WO₃ materials have been examined in this study. The sol-gel technique is used to prepare a thin layer coating of nano-TiO₂ on CNTs. The morphology of nano-TiO₂ coated CNTs are likes the pearl necklace structure. The thin film of CNTs/TiO₂ is deposited by spin coating technique to form a sensing film to measure the sensing properties. The sensing properties of the hybrid CNTs/TiO₂ indicate the decreasing the optimal operation temperature and the enhancing the

gas sensitivity for detecting CO gas at lower temperature. CNTs/WO₃ gas sensors have been synthesized by gas condensation method. The mean particle size of as-received WO₃ is 20 nm, and it is nucleated and grown after sintering treatment to 600 °C. The gas sensing properties of CNTs/WO₃ are examined in detecting the CO concentrations range from 120ppm to 600ppm and NO₂ concentrations range from 10ppm to 350ppm. The results indicate the hybrid CNTs/WO₃ sensor performs as a p-type MOS sensor behavior. The sensitivity of hybrid CNTs/WO₃ gas sensor (p-type) is obviously lower than that of pure nano-WO₃ (n-type) gas sensor at high operation temperature. While at the lower operation temperature such as 100°C the hybrid CNTs/WO₃ gas sensor can enhance the stability of gas sensor. Thus, it indicates the carbon nanotubes can help the nano-WO₃ gas sensor to adsorb the detected gas fast and stabilize the sensing at lower temperature.

4:00 PM **A2.7**

Pushing the limit of nanowire chemical sensing: selective detection of NO₂ down to ppb levels based on In₂O₃ nanowires. Daihua Zhang, Zuqin Liu, Chao Li and Chongwu Zhou; EEEP, University of Southern California, Los Angeles, California.

We demonstrate detection of NO₂ down to ppb levels using transistors based on both single and multiple In₂O₃ nanowires operating at room temperature. This represents orders-of-magnitude improvement over previously reported metal oxide film or nanowire/nanobelt sensors. A comparison between the single and multiple nanowire sensors reveals that the latter have numerous advantages in terms of great reliability, high sensitivity and simplicity in fabrication. Furthermore, selective detection of NO₂ can be readily achieved with multiple-nanowire sensors even with other common chemicals such as NH₃, O₂, CO and H₂ around.

4:15 PM **A2.8**

Metal Oxides Sub-Micron Wires for Gas Sensors. Elisabetta Comini¹, Patrizio Candeloro², Alessandro Carpentiero², Enzo Di Fabrizio², Camilla Baratto¹, Guido Faglia¹ and Giorgio Sberveglieri¹; ¹Chemistry and Physics Department, Sensor Lab, INFN, Brescia, Italy; ²LILIT-Beamline TASC-INFN, Trieste, Italy.

Nowadays continuous layers of polycrystalline Semiconductor Metal Oxide (SMO), such as SnO₂, WO₃ and TiO₂, are widely used in gas sensor technology [1]. The sensing mechanism allows to detect modifications in the external atmosphere by means of electrical measurements; in fact, due to the presence of different external gases, the SMO film changes its electrical properties, like the conductivity. On the other hand, their sensitivity is strongly grain-size dependent: the smaller the grain the larger the sensitivity [2]. In this work lithographic techniques combined with sputtering depositions are employed to fabricate polycrystalline SnO₂ and WO₃ gas sensors with controlled grain dimensions. The basic idea is to replace the continuous film with a pattern of wires in the sub-micron scale, thus having an upper limit for the lateral dimensions of the grains. As in sputtered SMO films the grain-size ranges from 30nm to 90nm [3], the width of the wires is required to be at least 100nm for having improvements respect to a continuous layer. It is worth to point out that at the working temperature of the sensors (200-500degC) the grains may present coalescence phenomena, thus changing their sensitivity; obviously in the case of 100nm wires these effects would be reduced. Moreover in a continuous and not porous film the grain-surface is only partially covered by the gas, thus having a limited sensitivity; instead, for the wires, the grain-surface is almost completely covered, the lateral walls of the wires being easily accessible. Two approaches were followed for the fabrication of the patterns: a simple lift-off process and a substrate patterning process. In the latter a silicon wafer covered with a 5micron-layer of silicon dioxide (SiO₂) is patterned by Electron Beam Lithography (EBL) and Reactive Ion Etching (RIE) techniques; the width of the SiO₂-wires is 100nm. Then the patterned SiO₂ is used as substrate for the deposition of 100nm SMO layer. Finally, electrical circuitry (connections for the sensing wires and heater circuit to reach the working temperature) is integrated on the device by means of optical lithography and lift-off process. For comparison analogous sensors with a continuous SMO layer were fabricated. The electrical characterization of the devices is a simple amperometric measurement: a potential difference is applied to the sensing element (SnO₂ wires or continuous film) and the electrical flow is measured in presence of different gases. The response of the sensors to different concentrations of several gases (CO, Ethanol, Acetone) was measured and a satisfactory improvement in the sensitivity was shown by the patterned sensors respect to the continuous-layer ones. [1] G.Sberveglieri, Sensors and actuators B 23 (1995) 103-109 [2] A.Dieguez et al., Sensors and actuators B 31 (1996) 1-8 [3] P.Serrini et al., Thin Solid Films 304 (1997) 113-122

4:30 PM **A2.9**

Electrospun Nanofiber-Based Fluorescent Sensors Using

Electrostatically Layered Polythiophenes. Xianyan Wang¹, Christopher Drew¹, Young-Gi Kim², Bon-Cheol Ku¹, Jayant Kumar¹ and Lynne A. Samuelson³; ¹University of Massachusetts Lowell, Lowell, Massachusetts; ²University of Florida, Gainesville, Florida; ³Natick Soldier Center, U.S. Army Soldier & Biological Chemical Command, Natick, Massachusetts.

Fluorescent conjugated polymers are known to show enhanced quenching versus small molecule fluorophores when interacting with an appropriate analyte species. This has been attributed to electron delocalization across more atoms than in smaller fluorophores, thus increasing the likelihood that the exciton interacts with an analyte species. We have previously demonstrated that sensing film performance may be enhanced by increasing the surface area using an electrospun nanofiberous structure instead of a continuous thin film. In this work we demonstrate a new fabrication approach by layering a conjugated polymer, hydrolyzed poly[2-(3-thienyl)ethanol butoxy carbonyl-methyl urethane] (H-PURET), onto the surface of an electrospun fiber membrane. This localization of the fluorophore to the surface of high surface area nanofiberous substrate resulted in significantly improved sensitivities compared to systems where the fluorescent polymer was distributed throughout the nanofibers. The fluorescence of these films could be quenched by extremely low concentrations of cationic electron acceptor analytes in aqueous solutions. This was attributed to both the high surface area to volume ratio of the films and the efficient interaction between the fluorescent polymer and the quenchers. The fluorescence quenching exhibited by such sensors exposed to methyl viologen and metal ions (Fe(III) and Hg(II)) showed a Stern-Volmer bi-molecular quenching relationship. The detection limits were in the range of a few tens of parts per billion. Fabrication techniques, characterization, and fluorescence quenching behavior of the sensors will be presented.

4:45 PM A2.10

Electrochemically Fabricated Conducting Polymer Nanoframework Electrode Junctions That Function as Resistive Sensors. Hsian-Rong Tseng, Jun Wang and Maksudul M. Alam; Molecular & Medical Pharmacology, UCLA, Los Angeles, California.

In this presentation, we will describe a template-free, site-specific, and scalable electrochemical method for the fabrication of individually addressable conducting polymer nanoframework electrode junctions in a parallel-oriented array. These conducting polymer nanoframeworks, which are composed of numerous intercrossing conducting polymer nanowires that have uniform diameters ranging from 40 to 200 nm, can be used for the chemical sensing of HCl and NH₃ gases and organic vapors and for sensing biological molecules in aqueous solutions.

SESSION A3/K4: Joint Session: Solid State Ionics-based Sensors

Chairs: Johannes Schwank and Enrico Traversa
Tuesday Morning, November 30, 2004
Republic B (Sheraton)

8:30 AM *A3.1/K4.1

A Titania Nanotube-Array Room-Temperature Sensor for Selective Detection of Hydrogen at Low Concentrations. Craig A. Grimes^{2,1}, Oomman K. Varghese^{2,1} and Gopal K. Mor^{2,1}; ¹Penn State University, University Park, Pennsylvania; ²Penn State University, University Park, Pennsylvania.

A tremendous variation in electrical resistance, from the semiconductor to metallic range, has been observed in titania nanotube arrays at room temperature, approximately 25°C, at ppm levels of hydrogen gas. The titania nanotube arrays are fabricated by anodizing a titanium foil or thin film in, typically, a hydrofluoric acid electrolyte with the diameter of the resulting nanotubes dependent upon the anodization voltage. For example, using a HF electrolyte a 10 V anodization voltage results in nanotubes of 22 nm inner diameter, while a 20 V anodization voltage results in 76 nm diameter tubes. Initially amorphous, the crystallinity of the nanotubes can be controlled by the temperature, time and atmosphere of a subsequent anneal. The crystalline nanotube arrays are coated with a 10 nm layer of palladium by evaporation, with Pt electrical contacts made by sputtering through a mask atop the Pd sensitized nanotube-array. At 25°C these sensors exhibit a resistance variation of the order of 104 in the presence of 100 ppm hydrogen, and a resistance variation of 106 to 1000 ppm hydrogen. Sensor resistance changes linearly from the lowest level we have been able to test, 20 ppm, to 1000 ppm, and then non-linearly to the explosive limit. The sensors demonstrate complete reversibility, repeatability, negligible drift, no hysteresis, and wide dynamic range. The sensors have a room temperature 90% response time of several tens of seconds, depending upon details of the

fabrication process. The nanoscale geometry of the nanotubes, in particular the points of tube-to-tube contact, is believed to be responsible for the outstanding hydrogen gas sensitivity. Furthermore, while reduction of nanotube diameter from 76 nm to 22 nm increases the surface area by a factor of two the hydrogen sensitivity is increased by approximately a factor of 200, hence the material architecture, not just surface area, plays a key role in determining the resultant properties. Cross-sensitivity testing on the titania nanotube sensors shows no response to CO, CO₂, and NH₃.

9:00 AM A3.2/K4.2

Resistive Oxygen Gas Sensors Using Cerium Oxide Nanosized Powder. Norimitsu Murayama, Noriya Izu, Woosuck Shin and Ichiro Matsubara; National Institute of Advanced Industrial Science and Technology, Nagoya, Aichi, Japan.

Resistive oxygen gas sensors operate based on the electrical conductivity of oxide semiconductor changing with the amounts of oxygen deficiency. The sensors are essentially suitable for low-cost production because of their small size and simple structure. The resistive oxygen gas sensors are promising candidates for electrical fuel injection control of two-wheel vehicles, which is necessary for responding to tightening two-wheel emission control regulations. Cerium oxide (CeO₂) is suitable material for the sensors, since it has large diffusion coefficient for oxygen. The response time of the sensor decreases with decreasing the powder size. Therefore, CeO₂ nanosized powder is necessary for fast response sensors. Cerium oxide nanosized powder was synthesized by modified precipitation method. The precipitate, which was formed from the addition of NH₄OH to Ce(NO₃)₃ aqueous solution, and was filtered. The obtained gel was mixed with carbon powder with a particle size of about 20 nm by a mechanically rotating mixer. The mixture was dried at 70 °C in air. The carbon powder was burned out by heat treatment at 900 °C in air for 4 h, resulting in the formation of granules of aggregated CeO₂ nanosized powder. The CeO₂ nanosized powder was easily disaggregated by ultrasonic vibration. Finally, the CeO₂ powder with a size of 50 nm was obtained. Using the powder, thick films were screen-printed on alumina substrates, and were fired at 1100 °C. The grain size was about 120 nm. The response time was about 20 ms at 800 °C.

9:15 AM A3.3/K4.3

Thermodynamic and Kinetic Principles for Electrochemical Gas Sensors based on Solid Ionic Conductors.

Evangelos D. Tsagarakis¹ and Werner Weppner²; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Faculty of Engineering, Christian Albrechts University, Kiel, Germany.

Several concepts can be applied for gas detection using solid ionic conductors. The fundamental characteristics and the essential variables for proper design of electrochemical cells are analyzed in terms of the sensing principle applied. The principal properties for materials as components of electrochemical devices are being illustrated. Employment of dynamic method allows implementation of the Fourier coefficients to generate a complex plane plot representation. This can be particularly useful for extracting information regarding the selectivity of an electrochemical cell to multiple gas species. Moreover, modeling the system response upon a periodical perturbation can be beneficial on understanding the individual processes and optimizing the overall performance.

9:30 AM *A3.4/K4.4

Non-Nernstian Planar YSZ-based Electrochemical Sensors with One Semiconducting Oxide Electrode.

Elisabetta Di Bartolomeo and Maria Luisa Grilli; Dept of Chemical Science and Technology, University of Rome Tor Vergata, Rome, Italy.

At present, non-Nernstian solid electrolyte electrochemical sensors seem to be the most promising devices for high temperature applications. Solid oxide electrochemical O₂ sensors are inexpensive and have successfully shown to work in harsh combustion exhaust environment. If modified to selectivity measure NO_x or CO/hydrocarbons concentrations, this type of sensors can be used to improve the combustion as a feed-back elements in engine control systems and thus comply with the always much more strict automotive emission regulations. Coating or undercoating one Pt electrode with semiconducting oxide powder with high catalytic properties in gas reduction/oxidation, it is possible to design devices with good selectivity and fast response time. Planar sensors based on tape-cast YSZ layers (150 μm of thickness) were fabricated. Two Pt finger electrodes were deposited on one side of the layers. One of the electrodes was covered with an oxide thick film. The oxide tested included WO₃, La_{0.8}Sr_{0.2}FeO₃ and In₂O₃. All the oxides were prepared using different chemical methods. The oxide powders were mixed with a screen-printing oil and thus painted on one metallic electrode. The sensors were tested in potentiometric devices at various

concentrations of NO₂ and CO (200-1000 ppm in synthetic air), at different temperatures. Amperometric and electrochemical impedance spectroscopy (EIS) measurements were performed to understand the sensing mechanism. Long-term measurements were carried out to investigate the stability of the sensors. Some field tests were also performed. Planar sensors were located close to a commercial oxygen sensor, downstream the three-way catalytic converter of a FIAT fire 1242 c.c. spark ignition engine coupled to a dynamometer. The gas sensor packaging used was like a commercial lambda probe provided with heating facility. Another commercial oxygen sensor was located upstream the catalytic converter to control the air/fuel ratio (A/F) of the engine. EMF response of gas and oxygen sensors both located downstream the catalytic converter were recorded simultaneously. The performance of the gas sensors was measured at the stoichiometric point (A/F=14) at different engine regimes (RPM and torque) and thus at different operating temperatures. To increase the NO_x concentration in the exhausts, some measurements at lean-fuel conditions (A/F>14) were also performed. The response of gas sensors was compared with the response of the commercial lambda probe. Moreover the EMF measurements were related to the exhaust gas concentrations measured by spectroscopic analytical equipment at the engine exhaust end: non-dispersive infrared spectrometer (NDIR) for CO and CO₂, chemiluminescence spectrometer for NO_x, and flame ionised detector (FID) for unburned hydrocarbons. Preliminary measurements showed promising results in terms of sensitivity, stability and reproducibility, even though the response time should be improved.

10:30 AM *A3.5/K4.5

Chemical Sensors for Automotive Applications.

Richard E. Soltis, Physical & Environmental Sciences, Ford Motor Company, Dearborn, Michigan.

Chemical sensors have become an essential part of the control system for vehicles powered by internal combustion engines (ICE). These sensors currently are used for feedback control of the air-to-fuel ratio (A/F) for improved vehicle performance and reduced emission levels. In addition, they also have been widely employed for monitoring the conversion efficiency, or 'health' of the catalyst as part of the on-board diagnostics (OBD) requirements. In the future, stricter emission standards and alternative powertrains (e.g. H₂ICE, fuel cells, lean burn, and hybrids) will undoubtedly require additional sensors for control and monitoring. At present, the oxygen sensor, which has been used universally for over 20 years, is the only exhaust gas sensor used on vehicles. It is one of the few sensors that can meet the stringent demands imposed by the extreme range of operating temperatures and harsh chemical environment of the automotive exhaust. This type of sensor is essentially a Nernst cell comprised of yttria-stabilized zirconia (YSZ) as the electrolyte (oxygen-ion conductor) with porous platinum electrodes. These sensors typically have an internal heater for rapid warm-up and to provide a more stable output signal. Recently, solid state electrochemical sensors for measuring NO_x have been developed for automotive applications. These sensors, also based on YSZ, consist of multiple oxygen pumping cells, with an integral heating element. Other materials for chemical sensing, including metal oxide resistors and SiC-based devices are also candidates for exhaust gas sensors. However, long term stability and durability concerns have resulted in limited implementation. Chemical sensors for other less-demanding applications, such as hydrogen leak detection or cabin air quality, are also of interest and are currently under development by several manufacturers. After a brief introduction to the basic operating principles of oxygen sensors, recent developments in electrochemical sensors, including planar sensor fabrication technology, will be described. The status of other zirconia-based sensors designed to measure gases such as NH₃, NO_x, HC, H₂O, and CO₂ will also be reviewed. Finally, chemical sensors based on other technologies will be discussed in light of current trends in emerging emission standards and alternative powertrains.

11:00 AM A3.6/K4.6

Humidity Sensing with Manganese Oxide Ambigel

Michael Scott Doescher, Jeremy J. Pietron, Jeffrey W. Long and Debra R. Rolison; Code 6171 Surface Chemistry Branch, NRL, Washington, District of Columbia.

Architecture is an essential element of sensor performance. Mesoporous electrically conducting birnessite manganese oxide is synthesized via sol-gel chemistry followed by evaporation of a nonpolar low surface tension liquid to prevent pore collapse. Ambigel nanoarchitectures have bicontinuous pore and solid networks that permit facile diffusion of analytes throughout the high-surface-area architecture. This combination of active nanoscale surface and full accessibility to analyte is especially appealing for gas-phase, temperature, and humidity sensors. The effects of electrode architecture were explored by characterizing both manganese oxide monoliths and sintered powder films (formed by drop casting ground ambigel on interdigitated array electrodes) to determine their

pore-size distribution (analysis of nitrogen physisorption data), thermal response, and the electrical response (impedance spectroscopy) under temperature and atmospheric control. Monolithic mesoporous manganese oxide nanoarchitectures exhibit a conductometric humidity response at equilibrium that is 17 times more sensitive than the sintered particulate film derived from the same material. As relative humidity increases, water condensation in the monolith creates an electrically wired pore-solid nanoarchitecture. Long-range continuity of the pore network in the ambigel permits proton conduction over macroscopic distances between measurement electrodes. The flux of protons in sintered powder samples of the same material is limited due to the disruption of proton conduction pathways at interparticle connections, thus limiting the sensitivity of the device to humidity.

11:15 AM A3.7/K4.7

Sr(Ti,Fe)O_{3-δ} exhaust gas sensors. Thomas Schneider, Christoph Peters, Stefan Wagner, Wolfgang Menesklou and Ellen Ivers-Tiffée; Institute of Materials for Electrical and Electronics Engineering, Universitaet Karlsruhe (TH), Karlsruhe, Germany.

In automotive applications oxygen sensors control the air-fuel ratio in order to reduce fuel consumption. Direct injection engines or lean burn engines operating with air excess ($\lambda > 1$) require more advanced sensor concepts [1]. Acceptor doped Sr(Ti,Fe)O_{3-δ} has been qualified as a resistive type oxygen sensor material [2], its electrical conductivity reflects the equilibrium between the oxygen partial pressure pO₂ in the atmosphere and the bulk stoichiometry at temperatures typically above 700 °C. SrTi_{1-x}Fe_xO_{3-δ} solid solutions were found to change their temperature coefficient of resistance (TCR) from negative to positive as iron increasingly substitutes for titanium, with the TCR tending towards zero at x = 0.35. This composition, Sr(Ti_{0.65}Fe_{0.35})O_{3-δ}, thus shows a temperature independent and, in contrast to donor doped compounds, a long term stable characteristic [3,4]. For the development of a planar type sensing element, Sr(Ti_{0.65}Fe_{0.35})O_{3-δ} has to be applied as a thick film on a zirconia substrate which has integrated Pt heating elements as well as Pt contacts [5]. Temperature independence (at T = 750...900 °C, pO₂ = 10⁻⁴...1 bar) and fast response times (t₉₀ = 6.5 ms at 900 °C), both key issues of Sr(Ti_{0.65}Fe_{0.35})O_{3-δ}, have to be maintained over the entire lifetime of the sensing element. In this work, financially supported by the Federal Ministry for Education and Research (Germany, BMBF PTJ-NMT 03N3102), the structural and electrical properties of the sensor are investigated with regard to the chemical stability of the sensing element. [1] E. Ivers-Tiffée et al., *Electrochimica Acta* 47 (2001), 807-814 [2] R. Moos et al., *Sensors and Actuators B* 67 (2000), 178-183 [3] W. Menesklou et al., *Sensors and Actuators B* 59 (1999), 184-189 [4] W. Menesklou et al., *MRS Symp. Proc.* 604 (2000), 305-310 [5] J. Riegel et al., *Solid State Ionics* 152-153 (2002), 783-800

11:30 AM A3.8/K4.8

A Study of the Electrical Properties and Stability of Sr(Ti,Fe)O₃ Thin Films for Oxygen Sensing Applications.

Scott J. Litzelman, Avner Rothschild and Harry L. Tuller; Crystal Physics and Electroceramics Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts.

In recent years, SrTi_{0.65}Fe_{0.35}O₃ (STF-35) has been studied in bulk ceramic and thick film form due to its unique temperature independent resistance above 700 C and pO₂ > 10⁻⁴ bar while retaining sensitivity to variations in pO₂ [1,2]. As a consequence of its unique properties, STF-35 has become a prime resistive oxygen sensor candidate for automotive exhaust systems. Recently, sensors fabricated from thick films were discovered to suffer from instabilities due to reaction between STF-35 and the alumina substrate upon which it had been deposited [3]. In this study, thin films of STF-35 are deposited on alumina and magnesia substrates and interaction products, if any, are investigated in detail in an attempt to identify a stable sensor-substrate combination. Preliminary measurements of the electrical properties of the film are also reported and compared with data obtained on bulk or thick film STF-35. To study the stability of STF-35 with respect to the substrate, thin films were deposited via pulsed laser deposition (PLD) onto alumina and magnesia substrates. X-ray diffraction analysis demonstrates that STF-35 reacts with alumina to form an intermediate reaction product, SrAl₁₂O₁₉. No such reaction was found when MgO substrates were utilized. Analysis by Rutherford Backscattering Spectrometry (RBS) does indicate, however, some depletion of strontium and iron near the substrate-film interface. The electrical properties of the films were studied using lithographically-designed microelectrodes in a newly-constructed microprobe chamber which allows for measurements in controlled atmospheres, up to temperatures of 1000 C. The thermal activation energies and response to changes in pO₂ are presented and discussed. REFERENCES [1] Menesklou, W., et al., *High temperature oxygen sensors based on doped SrTiO₃*. *Sensors and Actuators B*, 1999. 59: p. 184-189. [2] Moos, R., et al., *Materials for temperature independent*

resistive oxygen sensors for combustion exhaust control. *Sensors and Actuators B*, 2000. 67: p. 178-183. [3] Moos, R., et al., Temperature-independent resistive oxygen exhaust gas sensor for lean-burn engines in thick-film technology. *Sensors and Actuators B*, 2003. 93(1-3): p. 43-50.

11:45 AM **A3.9/K4.9**

High Temperature Operation and Stability of Languisite Resonators. Holger Fritze¹, Michal Schulz¹, Huankiat Seh² and Harry Tuller²; ¹Department of Physics, Metallurgy and Materials Science, TU Clausthal, Clausthal-Zellerfeld, Germany; ²Department of Materials Science & Engineering, MIT, Cambridge, Massachusetts.

High temperature stable piezoelectric materials such as languisite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) and gallium orthophosphate (GaPO_4) are attractive as the basis of gas phase chemical sensing at elevated temperatures. Specific surface affinity layers cause gas atmosphere dependent mass changes and, thereby, shifts in resonance frequency of piezoelectric resonators coated with such films. High sensitivity is expected since the mass sensitivity of e. g. languisite resonators at 800 °C has been shown to be on the same order of magnitude as that of quartz resonators at room temperature [1]. Factors limiting potential use of languisite as a gas sensor platform at elevated temperatures include excessive conductive and viscous damping, deviations from stoichiometry and chemical instability. We begin by summarizing the results of atmosphere dependent electrical conductivity and temperature dependent oxygen and gallium diffusivity data. A defect model consistent with these results points to oxygen ion transport dominant under oxidizing conditions shifting to electronic conduction under reducing conditions. Intentional doping of languisite single crystals is performed to modify the high temperature conductivity and piezoelectric properties of languisite. Based on a one-dimensional description of the resonator device, the material constants of the resonator are determined as a function of the temperature by fitting the calculated complex impedance to the experimental data in the vicinity of the resonance frequency. The effective viscosity of the resonator material and the bulk conductivity are found to control the resonator quality. The intentional doping suggests the possibility of lowering the damping by choosing the appropriate dopant concentrations. Based on the defect model, improvement of the resonance properties, i. e. lowering of damping at high temperatures, seems to be feasible. The rate of gallium loss from the surface at intermediate temperatures (750 °C), calculated based on the gallium diffusion data, is not believed to be of major concern regarding resonator performance. Conductivity degradation in hydrogen containing atmospheres is observed and the potential creation of reaction products is under investigation. [1] H. Fritze, O. Schneider, H. Seh, H. L. Tuller, G. Borchardt, High Temperature Bulk Acoustic Wave Properties of Languisite, *Phys. Chem. Chem. Phys.* 5, pp. 5207-5214, 2003.

SESSION A4: Modelling, Mechanism and
Structure-Properties Relationships
Chairs: Makoto Egashira and Ted Kamins
Tuesday Afternoon, November 30, 2004
Back Bay D (Sheraton)

1:30 PM ***A4.1**

Rational Synthesis and Optimization of Multifunctional Solid-State Gas Sensors. Johannes Schwank¹ and Ghenadii Korotcenkov²; ¹Chemical Engineering, University of Michigan, Ann Arbor, Michigan; ²Lab. of Microelectronics and Optoelectronics, Technical University of Moldova, Chisinau, Moldova.

A new approach is discussed for the rational synthesis and development of optimized multi-functional solid-state gas sensors. Multifunctionality, the incorporation of multiple types of reactivities into a material, such as acid and/or base functionalities, oxidation and/or reduction functionalities, etc., is a requirement in many gas sensing applications. The front end of many gas sensors contains catalytic layers, so that optimization of catalysts and optimization of gas sensors can be carried out in a synergistic fashion. Multifunctionality presents unique challenges to rational catalyst and sensor systems development because the overall performance of the material is a convolution of the performance of the various subcomponents, and optimization of these individual subcomponents in isolation does not necessarily lead to optimal, or even acceptable, overall performance. A major obstacle to dealing with these difficulties is the inherent complexity of heterogeneous systems prepared by traditional approaches, which makes it difficult to unambiguously identify the compositions and morphologies of the local active sites and their interactions. Further complicating the problem is the requirement to function in environments that can vary on both short and long time scales. A key to understanding, controlling, and optimizing these materials is the ability to produce

and study well-defined sensor materials with well-defined composition and morphology, with the flexibility to vary the composition easily without jeopardizing the structural uniformity. The development of new or improved materials for gas sensor applications requires a search for novel and innovative approaches to the nano-scale design of these materials. The use of the technology of surface modification by successive ionic layer deposition (SILD) method is such an innovative approach that will be discussed in this paper.

2:00 PM **A4.2**

A Novel Theoretical Model for Semiconducting Oxides Gas Sensors. Satyajit V. Shukla and Sudipta Seal; Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida.

Over the past several decades, extensive research has been undertaken over the globe to develop the gas sensors based on n-type semiconducting oxides. Different oxides such as tin oxide (SnO_2), indium oxide (In_2O_3), zinc oxide (ZnO), tungsten oxide (WO_3) have been utilized to sense various reducing gases (H_2 , CO, NO, NH_3 , H_2S). However, the theoretical understanding of the gas sensing behavior of these oxides has considerably lacked behind the material development. It has been recognized that the gas sensitivity, as well as the response and the recovery time of a sensor, depend on number of parameters, such as nanocrystallite size, film thickness, nature and amount of dopants, surface catalyst and foreign oxides, amount of film porosity, and operating temperature. Interestingly, a theoretical model, which would give the effect all these variables on the gas sensitivity has not been yet reported in the literature. Moreover, the development of a generalized equation, which would be applicable to all semiconducting oxides, is also lacking in the literature. In view of this, we propose here a new constitutive equation for the gas sensitivity of nanocrystalline semiconducting oxide sensors based on a single crystal model. The present theoretical model describes the relationship between the gas sensitivity, nanocrystallite size, film thickness, Debye length, operating temperature, the surface coverage, and lattice oxygen-ion-vacancy concentration. The validity of the proposed theoretical model will be justified by comparing the model predictions with the reported experimental results.

2:15 PM **A4.3**

Structure-Property Correlation in SnO_2 and Cr_2O_3 Aerogels. Sergei O. Kucheyev, T. van Buuren, T. F. Baumann, J. H. Satcher, T. M. Willey, R. W. Meulenber, T. E. Felter, L. J. Terminello and A. V. Hamza; Lawrence Livermore National Laboratory, Livermore, California.

Metal oxide aerogels—a somewhat extreme form of nanoporous metal oxides with undercoordinated surfaces—are open-cell solid foams derived from highly cross-linked wet gels by drying them under supercritical conditions. These materials are formed by nanometer size particles randomly interconnected into a solid network with a large degree of porosity and high surface area. Significant current interest in these novel nanoporous materials is fueled by their potential applications. In particular, novel surface properties or simply high surface areas in combination with low densities open up an opportunity to develop a range of high-performance devices such as gas- and bio-sensors, batteries, actuators, and catalysts. However, a major scientific challenge involves the understanding of the structure-property correlation and, especially, complex surface electronic properties of nanoporous metal oxides. Indeed, the electronic structure of these materials depends on porosity due to quantum confinement as well as surface relaxation and reconstruction effects, influencing device performance. In this presentation, we discuss the structural and electronic properties of low-density monolithic nanocrystalline SnO_2 and Cr_2O_3 aerogels synthesized using the epoxide sol-gel method recently developed in our laboratory. The electronic structure is studied by synchrotron-based soft x-ray absorption near-edge structure (XANES) and x-ray emission (XES) spectroscopies. In particular, we study the dependence of the element-specific partial density of states in the conduction and valence bands on porosity (or the undercoordinated surface atom fraction) and the size of ligaments of the nanofoam skeleton. We also compare our experimental results with previous molecular orbital and band structure calculations for full-density SnO_2 and Cr_2O_3 . Emphasis is given to understanding (i) the influence of the extremely high surface-to-volume atomic ratio on the electronic properties and (ii) the relationship between the partial density of electronic states (measured by XANES and XES) and the structural properties of foams. This work was performed under the auspices of the U.S. DOE by the University of California, LLNL under Contract No. W-7405-Eng-48.

2:30 PM **A4.4**

Environmental Sensitivity of Pentacene Thin-Film Transistors.* Mihaela Breban^{1,2}, Sergey Mezheny^{1,2}, Daniel R. Hines^{1,2}, Danilo Romero^{1,2}, Vincent Ballarotto² and Ellen Williams^{1,2}; ¹Physics, University of Maryland, College Park,

Maryland; ²The Laboratory for Physical Sciences, College Park, Maryland.

The sensitivity of organic thin film transistors (TFT) to environmental factors such as chemical impurities, charge transfer at interfaces, and grain boundaries is related to still incompletely understood mechanisms of transport. We have tested pentacene transistors in a carefully controlled environment that allows rapid changes in the gas phase composition. The response characteristic of transport, e.g. mobility and threshold voltage, are measured at room temperature and as a function of temperature with rapidly changing vapor composition. The transport results are correlated with direct probes such as Raman spectroscopy and photoconductivity spectroscopy. We measure a 50% decrease in source-drain current and a 2 V increase in threshold voltage within 10 s of when a pentacene TFT at room temperature is abruptly exposed to nitrogen (0.5 l/min) saturated with water vapor. Subsequent exposure of the device to dry nitrogen (0.5 l/min) leads to the source-drain current recovering to approximately 75% of its initial value (10^{-6} A), while the mobility and threshold completely recover. These observations, along with preliminary data from Raman spectroscopy, suggest that there is little or no chemistry occurring between water vapor and the pentacene. Photoconductivity spectroscopy (PCS) reveals the existence of broad band tails above the gap for transistors measured under ambient atmosphere. Correlation of the PCS results from both the Au-pentacene interface and the bulk pentacene as a function of water vapor exposure and gate voltage will be used to determine the difference in the density of gap states between the two areas.

*Supported by the Laboratory for Physical Sciences

2:45 PM **A4.5**

Temperature dependent conductivity of polyaniline nanofibers. Mei Xue¹, Mingqiang Bao¹, Kang L. Wang¹, Jiaxing Huang² and Richard B. Kaner²; ¹Department of Electrical Engineering, University of California, Los Angeles, Los Angeles, California; ²Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California.

The temperature dependence of the conductivity of polyaniline nanofibers doped with camphor sulfonic acid (CSA) has been investigated. Instead of using the traditional homogeneous aqueous solution of aniline, acid, and oxidant, the polymerization is performed in an immiscible organic/aqueous biphasic system, to separate the byproducts (inorganic salts, oligomers, etc.) according to their solubility in the organic and aqueous phases. It is found that $\ln \sigma(T)$ of the doped polyaniline nanofibers is about linearly proportional to T^5 . Compared to conventionally synthesized polyaniline where $\ln \sigma(T) \propto T^{1/2}$ or $T^{1/4}$, polyaniline nanofibers are much more sensitive to temperature. On the basis of detailed analysis of the structure characteristics, a three-dimensional conduction hopping - tunneling model is suggested to explain the experimental results. The sensitivity of the conductance to the doping concentration is also studied, which implies a method to control the conductivity of the polyaniline nanofibers. With much faster gas phase doping/dedoping times compared with conventionally cast films, these polyaniline nanofibers hold great potential for thermal sensor applications.

3:30 PM ***A4.6**

Gas Sensors Based on Semiconductor Oxides: Basic Aspects of Materials and Working Principles. Maria Cristina Carotta, Giuliano Martinelli, Cesare Malagu, Vincenzo Guidi and Alessio Giberti; Physics Department, University of Ferrara, Ferrara, Italy.

Since 1962 wide-gap semiconductor oxides have been of widespread interest owing to their peculiarity of modifying surface properties when interacting with reducing or oxidizing gases. Few years later, the first explosive gas sensor devices were fabricated and commercialized by Figaro Engineering Inc. Since then, a lot of efforts have been addressed to improve sensing properties, selectivity and reliability of semiconductor oxide gas sensors. Thousands of results have been reported about the characteristics and performance of sensors based on different materials; a case in point is tin dioxide, the most widely used material for gas sensing. The recent emphasis given to the research on nanostructures, leading to an enhancement in the surface-volume ratio, has opened the way to further improvement toward the sub-ppm gas detection. Therefore, atmospheric pollution monitoring has become sensible through semiconductor oxide gas sensors; however, selectivity is still the main hindrance to a reliable application, especially when a single sensor is used. At present, a method to select a specific material to detect a certain gas has not been identified yet; the selections are made on the basis of experimental data without the aid of a general model. For this purpose surface reaction chemistry and the link between the electrochemical potential, the density of states and the Schottky barrier have to be worked out. This work aims to analyze the most important semiconductor oxides for gas sensing, such as SnO₂, TiO₂, WO₃, LaFeO₃ and their modifications due to ion-addition or to

catalysers. The oxide powders, synthesized via wet chemical routes, have been characterized both as dispersed powders and as sintered films. Electron microscopy and X-ray diffraction have been adopted to observe the morphology, the crystalline structure and the mean grain radius. Deposition of the films was carried out through screen-printing technology. They have been studied comparing the electrical behavior under identical environmental conditions. Potential barrier heights have been measured via stimulated temperature measurements and density of ionized donors via Hall effect. A theoretical model has been developed to justify the size dependent behavior of nanocrystalline oxides. The model predicts grain-size gas sensing dependence for TiO₂ because of strongly radius dependent density of charged surface states, Nt. For SnO₂, instead, Nt results almost constant and thereby a modest dependence of the gas response on the particle size (ranging from 150 to 50 nm) is expected [1]. In general, the model predicts the Fermi level when the material can be considered as nanostructured, as confirmed by experimental evidence. Finally, a study to compensate the effect of the absolute humidity on the above materials, will be presented, too. [1] Cesare Malagu¹, Vincenzo Guidi, Maria Cristina Carotta, and Giuliano Martinelli, Applied Physics Letters 84, 4158 (2004).

4:00 PM **A4.7**

Sensing Mechanism of NO on Nanocrystalline Ru, Pt, Pd-doped SnO₂: Electron Paramagnetic Resonance, Mossbauer and Electrical Study. Franca Morazzoni¹, Claudio Maria Mari¹, Umberto Russo², Riccardo Ruffo¹, Marina Mattoni¹, Roberto Scotti¹, Carmen Canevali¹ and Luca Nodari²; ¹Scienza dei Materiali, University of Milano-Bicocca, Milano, Italy; ²Chimica inorganica Metallorganica e Analitica, University of Padova, Padova.

Transition metal doped semiconductor oxides films, prepared by sol-gel technique, not only are base materials for high sensitive small-dimension devices, but can also be used to provide further insight into the gas sensing fundamental phenomena. In the frame of a wide investigation concerning the interaction of different reducing gases with metal (Ru, Pt, Pd)-doped SnO₂, after the study on the CO [1,2] it is now proposed the interaction of the same materials with NO. The sensing mechanism was explored in the temperature range 373-623 K, using NO (500 ppm)/argon mixture. The structural surface changes of both SnO₂ and transition metal-doped SnO₂ were monitored by EPR (Ru³⁺ and Pd³⁺ centers) and Mossbauer (Sn²⁺ and Sn⁴⁺ centers) spectroscopies and compared with electrical measurements. Spectroscopic and spectromagnetic results demonstrated that the NO interaction generates electrons injection into the semiconductor oxide materials by the following mechanism: O_o (oxygen in oxide site) + NO = NO₂⁻ + e⁻ NO₂⁻ = NO₂ + V_o[·] (V_o[·] singly ionized oxygen vacancy, EPR active species) 2 O_o + NO = NO₃⁻ + 3 e⁻ NO₃⁻ = NO₂ + V_o[·] + O⁻ (V_o[·] doubly ionized oxygen vacancies) n V_o[·] + M⁴⁺ (Ru, Pd, Pt) = M⁽⁴⁻ⁿ⁾⁺ + n V_o[·] (n= 1-4 depending on the metal) (1) 2 V_o[·] + Sn⁴⁺ = Sn²⁺ + 2 V_o[·] (2) Electrons are transferred from the singly ionized oxygen vacancies, V_o[·], to tetravalent transition metal centers (reaction 1) and also to tetravalent tin centers (reaction 2), in the case of Pt-doped samples. Such electron transfer from V_o[·], to the metal centers, allows further electron injection into SnO₂ by NO. In fact, the values of the electrical sensitivity towards NO increase not only with the amount of the EPR active Ru³⁺ and Pd³⁺ centers but also when Sn²⁺ centers are present, as the case of Pt-doped samples. Chemisorbed NO₂⁻ and NO₃⁻ anions are probably responsible for the partial inhibition of the NO reductive effects, at temperature lower than 623K. It was concluded that a very important role in enhancing the electrical response of these materials is played by the indirect electron transfer mechanism from NO to SnO₂, through oxygen vacancies, which is suggested for transition metal-doped materials. [1] F. Morazzoni, C. Canevali, N. Chiodini, C. Mari, R. Ruffo, R. Scotti, L. Armelao, E. Tondello, L. Depero, E. Bontempi, Chemistry of Materials, 2001, 13, 4355-4361 [2] M. Acciarri, C. Canevali, C. M. Mari, M. Mattoni, R. Ruffo, R. Scotti, F. Morazzoni, Chemistry of Materials, 2003, 15, 2646-2650

4:15 PM **A4.8**

FTIR Analysis of the NOx Detection Mechanisms by Semiconductor Metal Oxides Nanoparticles. Marie-Isabelle Baraton¹ and Lhadi Merhari²; ¹SPCTS UMR CNRS, Univ. Limoges, Limoges, France; ²R&D, CERAMEC, Limoges, France.

Nitrogen oxides are particularly harmful to the environment because these primary pollutants are responsible for generating ozone. Due to their low cost, chemical sensors based on semiconductor metal oxides would allow the implementation of dense networks to efficiently and rapidly monitor nitrogen oxides concentration in urban areas and to track the pollution clouds. In previous works, we have already improved the performance of these chemical sensors in terms of sensitivity and detection thresholds by using nanoparticles in an optimized screen-printing fabrication process. However, the

fundamental mechanism of the nitrogen oxides detection is still a controversy. We report here the contribution of Fourier transform infrared spectroscopy to the understanding of the chemical reactions occurring at the nanoparticle surface when nitrogen oxides are adsorbed under the operating conditions of real sensors. These surface reactions are correlated with the variations of the electrical conductivity in the nanoparticles. Comparison of the reactivity to nitrogen oxides is made for different metals oxides including tin oxide, indium oxide and tungsten oxide.

4:30 PM **A4.9**

Gas Sensor Based on Reactive Ion Beam Assisted Deposition of MoO₃ Thin Films. Saket Gadia and P. I. Gouma; Materials Science and Engg., SUNY-Stony Brook, Stony Brook, New York.

This paper documents research on Reactive Ion Beam Assisted Deposition (RIBAD) of molybdenum trioxide thin films for gas sensing application. The primary plasma beam source is used to sputter material from the target, while the secondary is incident upon the substrate surface, have inlet of reactive gas such as oxygen and can be used as an ion assist source. The deposited material was annealed at 500 degree centigrade for 8 hours. The material phase and microstructure characterization was done by X-ray diffraction, Scanning electron microscopy and Transmission electron microscopy. Electrical property measurements and Sensing tests were performed at three different temperatures of 500, 450 and 400 degree centigrade under varying and constant concentration levels of ammonia and nitrogen dioxide gases. The importance of sensitivity, selectivity and stability has been represented by experimental results at different working parameters. The recorded data has been qualitatively and quantitatively analyzed and significant trends according to different parameters (processing methodology temperature, gas concentration) have been identified. This suggests relation between processing condition, the material property, response to gases at different concentration, and the optimum working temperature regime.

4:45 PM **A4.10**

HRTEM / EELS Analysis, Structural Characterization and Sensor Performances of Hydrothermal Nano-TiO₂. Ana Maria Ruiz¹, Jordi Arbiol², Albert Cornet², Kengo Shimanoe³, Joan Ramon Morante² and Noboru Yamazoe³; ¹Campus UAB, Centro Nacional de Microelectronica (IMB-CSIC), Bellaterra, Spain; ²Department of Electronics, University of Barcelona, Barcelona, Spain; ³Department of Materials Science, Kyushu University, Fukuoka, Japan.

Gas sensing requirements have claimed for sensing materials with very high active surface. Thus, materials with different methods based on modified sol-gel routes, laser pyrolysis, spray-pyrolysis ... have been applied during the last years which have satisfied the size requirements but not the material stability and, as a straightforward consequence, the gas sensor presents drifts, short lifetime and lack of stability. Usually, thermal treatments under different ambient conditions are applied which increases the sensor performances related to the material stability but paying a significant cost concerning active surface area and sensitivity characteristics. In this contribution we report the characteristics of the nano-TiO₂ obtained from a method based on a hydrothermal reactor using low synthesis temperatures (<200 °C), high pressure and controlled chemical solution parameters, such as the pH. The synthesized nano-TiO₂ presents small size, well defined and faceted surface, and such performances are slightly changed with the posterior temperature treatments up to 700 °C, maintaining anatase phase structure and grain size about 20nm. Detailed characterization data will be reported and their sensing consequences will also be discussed.

SESSION A5: Poster Session
Chairs: V. Dravid and G. Kiriakidis
Tuesday Evening, November 30, 2004
8:00 PM
Exhibition Hall D (Hynes)

A5.1

Sensing Behavior of Perovskites GdCo_{1-x}Cu_xO₃ Prepared by Solution and Ultrasonic-Assisted Aerosol Methods. Carlos R. Michel, Edgar R. Lopez, Mario C. Manzo and Arturo Chavez; Physics, C.U.C.E.I. Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

In recent years, oxides with perovskite-type structure containing cobalt have received considerable attention for their applications in fields like anodes for electrocatalytic methanol oxidation in fuel cells, ceramic membranes for oxygen permeation, etc. The most studied cobaltites with this structure have been the members of the solid solution: La_{1-x}Sr_xCoO₃. For these oxides, Sr-doping induce in

cobalt ions a mixed-valence state: +2 and +3, which enhance their physical and chemical properties. In the search of oxides having cobalt in a mixed-valence state, polycrystalline samples of GdCo_{1-x}Cu_xO₃ (x=0, 0.15, 0.3), were prepared from the dissolution of stoichiometric amounts of Gd(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O and Cu(NO₃)₂·5H₂O in aqueous media. These solutions were used in two synthesis routes: pyrolysis of dry precursors and ultrasonic-assisted aerosol. In the first method, the aqueous solutions were heat-dried at 76 °C, and the resulting powders were analyzed by DTA/TGA, to identify the temperature of formation of the perovskites. Further calcination in the temperature range from 100 to 950 °C was performed to obtain pure samples and to study their mechanism of formation. In the aerosol method a stream of droplets produced in an ultrasonic generator was passed through a tubular furnace heated at 950 °C. X-ray powder diffraction was performed in order to identify the target phases. Surface microstructure of powders was analyzed by SEM and show that solution method produced sub-micron semispherical particles and the aerosol method yield micron-sized hollow spherical particles. In order to determine their sensing capability, electrical properties of these oxides were tested in air, O₂ and CO₂; these measurements were made on pellets and thick films using the Van der Pauw four-point probe method. These results show a semiconductor behavior and selectivity from room temperature to 700 °C.

A5.2

Gas Selectivity of Polycrystalline Thick Films of SrPb_{1-x}Bi_xO₃. Carlos R. Michel, Gloria Santillan, Abraham Quino, Adalid Castillo, Rebeca Medina and Efrén Ballesteros; Physics, C.U.C.E.I. Universidad de Guadalajara, Guadalajara, Jalisco, Mexico.

In the search of new materials for gas sensing devices some factors are considered: reproducibility of preparation routes, operation temperature, gas selectivity and cost, could be among the most important. On the other hand, oxides with the perovskite-type structure have received a lot of attention due to their exceptional physical and chemical properties; about their transport properties, these expand from highly dielectric materials to superconductors. Some perovskites possessing a semiconductor behavior have been extensively studied, a particular case is the solid solution: La_{1-x}Sr_xCoO₃; this group of oxides are characterized to present oxygen non-stoichiometry, with strontium-doping producing cobalt ions in a mixed-valence state +2 and +3. Due to their properties, members of this solid solution have been successfully applied as cathodes for nitric oxide reduction, ceramic membranes for oxygen separation, electrodes in electrocatalytic methanol oxidation, etc. Taking into account that a mixed valence state is related with the transport properties of perovskites, and this could favor gas sensitivity, in this work, polycrystalline samples of SrPb_{1-x}Bi_xO₃ (x = 0, 0.1) were prepared from the dissolution of stoichiometric amounts of Sr(NO₃)₂, Pb(NO₃)₂ and Bi(NO₃)₃ in aqueous media. Aliovalent substitution in this solid solution gives lead ions in a mixed valence state: Pb⁺², Pb⁺⁴. For the preparation of the oxides the solutions were slowly heat-dried at 65 °C obtaining dry precursors; these were analyzed by DTA/TGA to identify the temperatures of formation of the perovskites. Calcinations in the temperature range from 110 to 650 °C were performed to obtain pure samples. X-ray powder diffraction was used to study the mechanism of formation of the target oxides. Surface microstructure of powders was analyzed by SEM and show that the preparation procedure yields agglomerations of sub-micron particles. The powders were finely ground and mixed with acetone to form thick-films, which have a thickness of approximately 70 μm. D.C. electrical conductivity vs. temperature curves (in air), show a semiconductor behavior with two well defined slopes. In order to determine their sensing capability, electrical measurements were performed in O₂ and CO₂; the results show an enhanced gas sensitivity at specific temperatures below 600 °C.

A5.3

Temperature Independent Semiconducting Metal-Oxide Oxygen Sensors. Avner Rothschild¹, Scott J. Litzelman¹, Harry L. Tuller¹, Wolfgang Menesklou², Thomas Schneider² and Ellen Ivers-Tiffée²; ¹Department of Materials Science & Engineering, MIT, Cambridge, Massachusetts; ²Institut für Werkstoffe der Elektrotechnik, Universität Karlsruhe, Karlsruhe, Germany.

Oxygen sensors are widely used in automotive exhaust gas control systems for optimization of fuel combustion and conversion of deleterious combustion products such as CO, hydrocarbons, and NO_x to safer gases such as CO₂, H₂O, and N₂ by way of the three way catalyst. The oxygen sensors market is dominated by electrochemical ZrO₂-based sensors.¹ The more common potentiometric sensor has a simple and robust design but is effective only over a narrow range bordering the stoichiometric air/fuel ratio where there are large variations in oxygen pressure. Amperometric oxygen sensors extend operation to lean conditions, but their design is considerably more complex. Possible alternatives to ZrO₂-based oxygen sensors are resistive-type sensors based on semiconducting oxides such as TiO₂.²

These sensors are sensitive to oxygen pressure and have a relatively simple design. However, their response is typically complicated by cross sensitivity to temperature. Efforts have thus been directed towards finding materials with temperature independent oxygen pressure sensitivity.³ SrTi_{1-x}Fe_xO_{3-δ} (STF) solid solutions were found to change their temperature coefficient of resistance (TCR) from negative to positive as iron increasingly substitutes for titanium, with the TCR tending towards zero at x = 0.35.⁴ This composition, SrTi_{0.65}Fe_{0.35}O_{3-δ} (STF35), thus becomes a prospective oxygen sensor candidate for automotive applications. In this work, we investigate the TCR behavior of STF solid solutions. Starting from the general expression for the electrical conductivity for these p-type oxides (at high oxygen pressures), $\sigma = q\mu p$, we derive the conditions for zero TCR. One of the key requirements is that the Fermi energy lie close (within a few tenths of an eV) to the valence band. By analyzing conductivity measurements as a function of oxygen pressure and temperature for different STF compositions, we show that the bandgap energy changes as a function of the iron content, decreasing from 3.2 eV for SrTiO₃ to 1.9 eV for SrFeO₃. Complementary measurements including Hall effect, photoelectron spectroscopy, and optical spectroscopic measurements are presented, and the defect chemistry of STF is discussed in light of these results.¹ J. Riegel *et al.*, Solid State Ionics 152-153 (2002) 783. ² E. M. Logothetis, Ceram. Eng. Sci. Proc. 1 (1980) 281. ³ P. T. Moseley, Sens. Actuators B 6 (1992) 149. ⁴ W. Menesklou *et al.*, Sens. Actuators B 59 (1999) 184.

A5.4

Performance of a MIS Type Pd-Cr/AlN/Si Hydrogen Sensor. Linfeng Zhang⁴, Erik McCullen³, L. Rimai⁴, R. Naik³, Ron Baird⁴, G. Newaz², Gregory W. Auner⁴ and Simon Ng¹; ¹Chemical and Material Science, Wayne State University, Detroit, Michigan; ²Mechanical Engineering, Wayne State University, Detroit, Michigan; ³Physics and Astronomy, Wayne State University, Detroit, Michigan; ⁴Electrical and Computer Engineering, Wayne State University, Detroit, Michigan.

For safe and efficient use in leak detection and process control, hydrogen sensors should have high sensitivity, but also should be able to continuously operate over a wide range of hydrogen concentrations. In previous research, a metal-insulator-semiconductor (MIS) type sensor, utilizing a Pd/AlN/Si structure was shown to be sensitive to hydrogen concentrations in the surrounding flow as low as 1ppm. However, it showed response baseline drift and saturation around 50ppm. In order to develop a more stable MIS type sensor with wider dynamic range, up to the lower explosive limit of 4-*vol* %, Pd-Cr alloy gates were used instead of the pure Pd gates previously employed. These alloy gates were deposited by magnetron sputtering using varying Cr compositions, from 2-13% measured using x-ray photoelectron spectroscopy, and varying thickness. We have investigated the electrical characteristics, sensitivity, and response time of these Pd alloy sensors. The use of the alloy gates not only extended the dynamic range of the response to hydrogen concentrations between 100ppm and 50,000ppm flow, but also showed shorter turn on/off response time. Also, various film structures such as Pd, Pd/Pd-Cr, Pd-Cr, and Pd-Cr/Pd were also studied. The addition of Cr suppresses the morphology change of the Pd-Cr film, studied using atomic force microscopy. The data suggests that the outer surface of the Pd alloy film determines the sensor's dynamic range, and the interface between the alloy film and the AlN determines the sensor's response amplitude and sensitivity. Finally, more than 2 active sites on alloy surface are needed to dissociate a hydrogen molecule.

A5.5

Abstract Withdrawn

A5.6

Formation of Porous Silicon Layers on Insulating Substrate for Microbridge-Type Sensor Applications. Leonid Balagurov¹, Sergey Andrushin², Susan Bayliss³, Galina Liberova², Elena Petrova¹, Bayram Unal³ and Dmitry Yarkin¹; ¹Institute of Rare Metals, Moscow, Russian Federation; ²Unitary Enterprise Center ORION, Moscow, Russian Federation; ³Solid State Research Centre, De Montfort University, Leicester, United Kingdom.

Porous silicon (PS) is an excellent material for its use as a sacrificial layer (SL) in fabrication process of membranes, bridges, cantilevers and other complicated constructions required for such micromachined devices as gaseous sensors, pressure detectors, capacitive microphones, thermopiles, etc. Enormous area of the pores provides rapid room-temperature removal of this PS-made SL. Traditional technology of PS fabrication based on anodization process of crystalline silicon (c-Si) allows to obtain PS layers of different thickness and porosity. However, there are some applications (microbolometer and others sensors arrays) where SL would cover Si₃N₄ and SiO₂ insulating layers having high electrical resistance. Polyimide, usually used as SL for microbolometers is not stable at above 450 °C. This work describes

two methods, which allow to form thermally stable PS on insulating layers. PS was made from polycrystalline silicon (poly-Si) layer with grain size of 200-400 nm deposited by LPCVD method on insulating, chemically stable Si₃N₄ layer. Poly-Si was doped by ion implantation or diffusion of boron and has resistivity of 2 - 0.003 Wcm. Typical starting multi-layer structure was poly-Si(1.6-2.7 μm)/Si₃N₄(0.2 μm)/SiO₂(0.2 μm)/c-Si. The first method proposed for PS SL formation is modified electrochemical etching: anodic current flows from the top electrode through electrolyte/poly-Si junction and then laterally, along poly-Si layer until counter electrode. We find that homogeneous PS layer with smooth surface is formed from heavily doped p-type poly-Si. Lower doping level of poly-Si leads to large variation of PS thickness along the lateral direction. Moreover, the anodization of low-doped p-type poly-Si results in appearance of rapidly growing macropores. The second method proposed is chemical (stain) etching. In past the drawback of stain etching was relatively low (close to one hundred nanometers) thickness of resulting porous layer and formation of the deep crater from above the layer. We overcame noted problems utilizing HF:HNO₃ etching solutions with low concentration of HNO₃. Besides, HBF₄ and NaNO₂ were used to vary the porosity and etching rate. Addition of surfactants allowed to avoid sticking of gas bubbles to etched surface and thus improve the surface quality. PS SL prepared have sufficiently high (about 60%) porosity and smooth surface (the roughness was below 10 nm). Si₃N₄ bridges were made on PS by standard lithography technology, and finally PS SL were removed in KOH solution.

A5.7

Fabrication of Vapor and Gas Sensors Using Films of Aligned CNx Nanotubes. Federico Villalpando^{1,2}, Aldo Romero², Emilio Munoz-Sandoval², Luis Miguel Martinez¹, Humberto Terrones² and Mauricio Terrones^{2,1}; ¹Departamento de Física y Matemáticas, Universidad Iberoamericana, Mexico City, Mexico; ²Department of Advanced Materials, IPICYT, San Luis Potosí, S.L.P., Mexico.

We have succeeded in sensing rapidly (0.1 – 0.5 sec response), relatively low concentrations of toxic gases, and organic vapors (e.g. acetone, ethanol, gasoline, pyridine, chloroform, etc.) using electric devices integrating films and compressed pellets of aligned CNx nanotubes. We demonstrate, for the first time, that CNx nanotubes could be more efficient for monitoring toxic and hazardous species, when compared to pure carbon nanotubes. This is due to the fact that CNx nanotubes exhibit nitrogen rich islands on their surface, which are highly reactive. Using first principles calculations we confirmed that pyridine-type regions on the tube surface bind strongly (chemisorption) to ammonia, acetone and OH groups, thus altering their density of states (DOS) and minimizing the electron conduction causing a decrease in the states around the Fermi energy (Ef). The fabricated sensors are sensitive to physisorption and chemisorption when exposed to different gaseous species. Our results demonstrate that CNx nanotubes could be used as fast responsive sensors due to the nitrogenated sites on the tube surface, thus opening novel avenues in the sensor industry especially in the fabrication of reusable alcoholmeters.

A5.8

Vitreous Chalcogenide Semiconductors for Gas Sensing Application. Igor Dementiev¹ and Serghei Dmitriev²; ¹of Physics, Moldova State University, Chisinau, Moldova; ²of Industrial and Environmental Chemistry, Moldova State University, Chisinau, Moldova.

Report presents results of research aimed the investigation of possibility to use such chalcogenide materials as vitreous As₂S₃, As₂Se₃ and their solid solutions for gas sensors applications. For a long time these materials were well-known as materials mostly used for optical information registration. Developed approach allows to widening the sphere of application of given materials and create new class of gas sensitive devices. Thin film gas sensitive elements on the base of solid solutions of (As₂S₃)_x-(As₂Se₃)_{1-x} (where x=0; 0.3; 0.5; 0.7 and 1.0) were obtained by means of the thermal evaporation under vacuum conditions 10⁻⁵ Torr. Thin films can be deposited on both hard and flexible substrate. Formed films had specific resistance on the level 10¹⁰-10¹⁴ Ohm.cm (on dependence on composition) at the thickness of 1-2μm. Gas sensitivity S of CGS thin film was determined as ratio of sheet conductivity G measured in pure air and in the presence of gas impurity in atmosphere (S=(G_{gas}-G_{air})/G_{air}). Measured sensitivity amounted 2-3 relative units for CO and 7-8 for hydrogen at the 100 ppm concentration levels of both gases in atmosphere. It is important to note that all measurements of gas sensitivity were performed at room temperature that allows, in comparison with traditional metal oxide based gas sensors, to excluding the heater from the construction of gas sensors and decreasing through that both manufacturing and operational cost. Also, it is well-known another merit of given materials - their high radiation resistance. So, it may be concluded that chalcogenide semiconductor materials can be considered as perspective materials

for gas sensor application, including for space application. However, the mechanism of the gas sensitivity is not clear still and requires further investigation.

A5.9

Mechanism of the Oxygen Interaction with a Surface of Thin Nanosized Metal Oxide Film. Vladimir Brinzari¹, Ghenadii Korotcenkov¹ and Serghei Dmitriev²; ¹of Microelectronics, Technical University of Moldova, Chisinau, Moldova; ²Industrial and Environmental Chemistry, Moldova State University, Chisinau, Moldova.

This paper presents result of investigation of the oxygen behavior at the interaction with a surface of semiconductor metal oxide film. The idea to carry out such research is connected with the key role, which oxygen plays in the processes of impurity gas molecules detection in atmosphere and semiconductor surface sensibilization. Numerical modeling of the interaction was carried out for different temperatures and oxygen partial pressures. Results of modeling are compared with the results of experimental study of oxygen-semiconductor film system. The analysis of the equations describing the rates of reactions of dissociative adsorption has allowed to establishing general expression for concentration of oxygen chemisorbed on the surface of semiconductor. Also, there was established the interconnection of the oxygen concentration and tin film conductivity, which is described by the power dependence on surface concentration of oxygen in neutral form. Numerical simulation of transient processes on the surface of semiconductor in the presence of oxygen has shown that kinetic processes of gas sensing are determined by the second order adsorption/desorption reactions of oxygen. At that the kinetics of the quasi-interaction with surface befalls under conditions of the quasi-equilibrium between conduction band electrons and oxygen chemisorbed on the surface. Time constants of transient processes are determined by the rates of adsorption/desorption of oxygen in its neutral form. Transient response curves are closed to exponent but the transient recovery curves demonstrate more complicated form. Basic results of numerical simulation have demonstrated very good coincidence with experimental data.

A5.10

Influence of the Carbon on Tin Dioxide Films Gas Sensitivity. Vladimir Brinzari¹, Ghenadii Korotcenkov¹ and Serghei Dmitriev²;

¹Department of Microelectronics, Technical University of Moldova, Chisinau, Moldova; ²Industrial and Environmental Chemistry, Moldova State University, Chisinau, Moldova.

Our report presents results of investigations aimed the improvement of gas sensitive characteristics of gas sensors on the base of tin dioxide thin films and consider, from this point of view, the influence of carbon atoms on the sensing process. Our experiments have shown that SnO₂ films deposited from water solution of SnCl₄·5H₂O already possess sufficient sensitivity to 0.5% vol. of CO in air whereas films deposited from alcohol (ethanol) solution need for additional doping with Pd that to provide acceptable level of sensitivity. Such behavior of thin tin dioxide films has determined the necessity to conduct comparative analysis of the surface state, which was made on the base of results of SIMS investigations of undoped tin dioxide films obtained both from water and alcohol solutions. SIMS spectra demonstrate the presence of abundance of species, including O, C, CH, CH₂, OH, Ca, Mg, Cr, Cl, Fe and others, more complicated hydrocarbons (C_nH_m), on the surface of SnO₂. It was established that amplitudes of these peaks depend on regimes of deposition and qualitative and quantitative composition of surface impurities, which depends, in its turn, mainly on the type of used solvent and in less degree, as it could be expected, on temperature of deposition. For films deposited from alcohol solutions the dominating peaks were bounded with presence of carbon and its hydrocarbon compounds. On the base of obtained results the role of carbon in passivation of active adsorption centers is discussed and the conclusions regarding further improvement of technology of high sensitive thin film preparation are made.

A5.11

Surface Plasma Treatment and Sensibilization of Tin Dioxide Films for Enhancement of Gas Sensitivity and Selectivity.

Vladimir Brinzari¹, Ghenadii Korotcenkov¹ and Serghei Dmitriev²;

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This paper presents result of investigation aimed the improvement of gas sensitive characteristics of gas sensors on the base of tin dioxide thin films through the treatment of the last ones in high frequent (HF) oxygen plasma and surface doping of tin dioxide films. As object for investigation tin dioxide thin films deposited by chemical spray deposition process were used. The thickness of films was varied in the range 20-100 nm. Films were deposited at the temperatures in interval

400-500°C from alcohol solutions of SnCl₄·5H₂O. Surface treatment of obtained tin dioxide layers was carried out in pure oxygen plasma at room temperature. Time diapason of treatment had been varied from 5 to 45 minutes and optimal time for such treatment of tin dioxide thin films was determined. At that, the resistance and, as result, gas sensitivity grows 3-4 times. The changes in these parameters are discussed from the point of view of alteration of thin film's stoichiometry, for control of which there were used IR and SIMS measurements. Obtained results are compared with results of experiments on thermal annealing in oxygen atmosphere at high temperatures (~600°C). Another way to increase gas sensitivity of thin film's gas sensors is surface sensibilization through doping. As dopants there were used Pd and Cu also deposited by chemical spray pyrolysis method from the solutions of corresponding salts (PdCl₂ and CuCl₂·2H₂O) on the surface of tin dioxide films. Such modification of surface of tin dioxide films has allowed to increasing of sensitivity to H₂ up to 5·10³ rel. units (high selectivity) at the simultaneous shift of sensitivity maximum from 350 to 150°C. Using of Cu, in its turn, has allowed to provide selectivity and 4-5 times sensitivity increase of obtained films to CH₄ and C₃H₈ presence in atmosphere. At that, operating temperatures decreased from 500-520°C to 350-370°C. It is concluded that combination of HF oxygen plasma treatment and surface sensibilization through surface doping is an effective way to considerably improvement of gas sensitive and selective characteristics of tin dioxide based thin film gas sensors.

A5.12

Chemical Synthesis, Characterization and Gas-Sensing Properties of Thin Films in the In₂O₃/SnO₂ System.

Mauro Epifani¹, Luca Francioso¹, Antonella M. Taurino¹, Pietro Siciliano¹, Raul Diaz² and Joan R. Morante²; ¹CNR-IMM, Lecce, Italy; ²Departament d'Electronica, Barcelona University, Barcelona, Spain.

The utilization of additive elements to the active material in gas-sensing devices is a usual procedure, aiming at improving the device performance, in particular as concerns its selectivity and response time. In this sense the additive acts as a catalyst, but it must be taken into account that it may also influence the intrinsic properties of the sensing layer, from the grain size to the surface morphology and to the electrical conductivity. Thus, both from a fundamental and a device-oriented perspective, it is of interest to explore the influence of the additive concentration on the sensor properties and performances. In the case of thin-films based devices, the physical deposition techniques hardly allow to control the additive concentration and its distribution in the active layer. Very recently, an increasing interest has been emerging in the chemical deposition of thin films for gas-sensing devices, and the problematic of introducing varying additive amounts in the active material is particularly suited to be faced with such techniques. Moreover, it is possible to start from nominal compositions that are not allowed by the phase diagrams of the two components, and to investigate the possible formation of heterostructures of the two oxides on a nanometric scale. In this work, the change in the sensor properties and performance were studied by focusing on In₂O₃ and SnO₂ thin films, both pure and containing different relative concentrations of the two oxides. The films were deposited by sol-gel and solution processes. The films for the physical characterization were deposited onto oxidized silicon substrates, while the films for the gas-sensing tests were deposited onto alumina. The films on alumina were heat-treated at 500°C before device processing. The films on silicon, heated at various temperatures, were characterized by FTIR spectroscopy, X-ray diffraction and SEM observations. The interaction between the two systems is particularly evident in the case of the system described by a 50% In₂O₃-50% SnO₂ nominal composition. The crystallization on In₂O₃ during the film heat-treatment hinders the crystallization of SnO₂, thus Sn is dispersed as an n-dopant in the In₂O₃ lattice, indeed showing a current signal, in the gas-sensing test, two orders of magnitude higher than the pure film. The response of the mixed-oxide based device to NO₂ is better than pure In₂O₃, indicating a possible role of Sn in catalyzing the reactions at the gas-film interface. On the other hand, the response (relative resistance change) of pure SnO₂ to low (0.1 ppm) NO₂ concentrations ranges from 150 to 300, a result that can be correlated with the nanostructure of the film, which, from SEM and XRD results, seems constituted by very small grains. This is a result of the synthesis process, based on a novel precursor and, by itself, is an outstanding feature of this work. Further results of gas-sensing tests for various compositions of the mixed system will be presented.

A5.13

Preparation of TiO₂ Micro Wire Sensor Prepared by Phase Separation-Selective Leaching Method. Atsuo Yasumori, Jun

Yoshida, Hayato Matsumoto and Keishi Nishio; Department of Materials Science and Technology, Tokyo University of Science, Noda-shi, Chiba, Japan.

The practical gas sensors generally comprise oxide semiconductor fine

particles such as SnO₂ and TiO₂, and in recent applications, those are required much higher sensitivity for low concentration of hazardous gaseous substances and much faster response time for internal-combustion engines. The present sensors have porous body, which are prepared by conventional sintering process of raw oxide fine particles, in order to achieve a high surface area. On the contrary, there are some disadvantages of such porous materials, that is, slower response time due to long diffusion paths in the sensors and decrease of sensitivity due to strong adhesion of target gaseous substances inside the sensors. Thus, micro porous body of oxide semiconductors is required in order to make response time faster and sensitivity higher. Some silicate systems such as TiO₂-SiO₂ binary system have stable immiscibility region above their liquidus temperatures. When their high temperature melts were held in their immiscibility regions, the melts separate into two liquid phases. This phase separation phenomenon is very effective in the preparation of composite materials, which consist of TiO₂ rich phase comprising nanometer-scale fine TiO₂ particles and SiO₂ rich phase as glassy matrix. Thus, TiO₂ porous materials are possible to be formed by quenching of phase separated melt and subsequent selective leaching of SiO₂ glassy matrix. Furthermore, it is easy to control the shape of the material by deformation of the melt during quenching. In this study, porous TiO₂ micro wire comprising nanometer scaled TiO₂ fine particles were prepared by quenching with fiber drawing technique, and subsequent selective leaching process. The obtained porous TiO₂ micro wire showed several-tens to one hundred micrometer in diameter. The micro wire comprised several tens nanometers size of primary TiO₂ particles in needle-like shape, which were oriented along the wire axial direction. The electro conductivities of the micro wires increased with increase of the amounts of TiO₂ component in starting composition. Their conductivities also increased with temperature. These results indicated that the appropriate micro wires had continuous phase of TiO₂ fine particles and showed semiconductor behavior. The gas sensing ability was evaluated by change of electro conductivity in flowing conditions of various rarefied gases such as hydrogen and some volatile organic compound. The electro conductivity steeply decreased with increase of concentrations of gaseous substances within appropriate range. The response time was much faster than that of the porous disk-shaped samples which prepared the similar process. Thus, this micro wire sensor has a potential for some practical applications.

A5.14

Electrical Conductivity of HgTe at High Temperatures.

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The electrical conductivity of HgTe was measured using a rotating magnetic field method from 300 K to the melting point (943 K). A microscopic theory for electrical conduction was used to calculate the expected temperature dependence of the HgTe conductivity. A comparison between the measured and calculated conductivities was used to obtain the estimates of the temperature dependence of Γ₆-Γ₈ energy gap from 300 K to 943 K. The estimated temperature coefficient for the energy gap was comparable to the previous results at lower temperatures (≤ 300 K). A rapid increase in the conductivity just above 300 K and a subsequent decrease at 500 K is attributed to band crossover effects. This paper describes the experimental approach and some of the theoretical calculation details.

A5.15

SnO₂ : Fe₂O₃ Nanostructured System as Semiconductor Gas Sensor Material.

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Introduction Metal additive introduction in nanostructured metal oxides used as base materials for semiconductor gas sensors, is of great interest due to the influence on their physical and chemical properties. On one hand, these additives can modify the catalytic properties, and the sensitivity and selectivity of the base material in the electrical response in front of a gas [1]. On the other hand, the presence of these additives, also has influence on the morphology and grain size of the generated nanostructures [2, 3], as well as in the formation of new phases (metal oxides or metal binary compounds), leading to a substantial modification of the base material properties. On this way, the addition of several noble and transition metal oxides to tin oxide has been reported as an essential step in the production of reliable chemical sensors. In the present work, we report a detailed study based in transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) of the nanometric binary system

SnO₂:Fe₂O₃ microscopic structure and composition. Samples were grown by sol-gel technique. Results and discussion By adding Fe₂O₃ to the base SnO₂ we obtain a clear decrease on the nanoparticle grain size (up to 3 nm diameter). The presence of Iron has an inhibiting effect on the nanoparticles growth. Moreover, the increase in iron concentration affects the SnO₂ internal structure, leading to a SnO₂ lattice distortion. SnO₂ lattice parameters decrease when increasing the additive concentration from 0 to 10%. EELS analysis reports an Iron ultradispersion, this and the former results, suggest the formation of a binary alloy. This latter result has been analyzed by means of high-resolution electron microscopy and several atomic models and computer simulations have been carried out in order to confirm results. References [1] A. Cabot, J. Arbiol, J.R. Morante, U. Weimar, N. Barsan, W. Gopel. *Sensors and Actuators B*, 70, (2000) 87. [2] J. Arbiol, A. Cirera, F. Peiro, A. Cornet, J. R. Morante, J. J. Delgado and J. J. Calvino, *Appl. Phys. Lett.*, 80 (2), (2002) 329. [3] J. Arbiol, J. Cerda, G. Dezanneau, A. Cirera, F. Peiro, A. Cornet, J. R. Morante, *J. Appl. Phys.*, 92(2), (2002) 853.

A5.16

A Carbon Nanotube FET as a Platform for the Development of New Sensors: Products, Specifications and Perspectives.

Jean-Christophe P. Gabriel, Nanomix, Emeryville, California.

The mission of Nanomix is to develop and commercialize chemical and biological sensors based on a technology platform that integrates carbon nanotubes into silicon microelectronics. Nanomix has developed a new sensing technology based on nanoelectronic components. Each device contains carbon nanotube based FET sensors that are modified to respond specifically to various chemical or biological species. The nanosensor chip features state-of-the-art performance in a tiny package that consumes very little power. These inexpensive nanosensors will enable a new generation of research tools and the deployment of wireless sensor networks to replace more costly chemical sensors in many applications. In this presentation we will report the progress of Nanomix toward the production and commercialization of our first product: a hydrogen sensor, which is currently in external customer trials. We will report on its technical aspects as well as on its product specifications. We will also present our progress in the development of the FET itself as a generic platform for the development of new sensors This work was supported by NSF SBIR grant 0340484.

A5.17

Conducting Polymeric Nanocomposite for Ammonia Gas Sensor Applications.

Arun Kumar, Brian Brantley, Souheil Zekri and Ashok Kumar; Nanomaterial and Nanomanufacturing Research Center, University of South Florida, Tampa, Florida.

Ammonia gas presents many hazards to both humans and the environment. Due to its highly toxic characteristics, even low level concentrations (ppm) of ammonia gas pose a serious threat. As a product of global population growth, an increased number of human lives are being endangered by the effects of ammonia gas exposure. Ammonia gas is a byproduct of many industrial processes such as fertilizer manufacturing, chemical manufacturing, and livestock farming. Current ammonia sensing devices allow for the detection of lower level (ppm) ammonia gas presence. However, these sensors suffer from low selectivity, lower sensitivity and require high temperatures. A new approach is needed to improve the selectivity and sensitivity for ammonia gas detection. In the present approach a method has been explored to enhance sensor performance. Conductive polymers combined with selected metal oxides and carbon nanotubes have been tested for ammonia gas sensing applications. Polyaniline was doped with tin oxide and carbon nanotubes to increase the porous structure as well as the number of binding sites for gas molecule interactions. The proposed modified conducting polymeric nanocomposite increased the sensitivity and selectivity for ammonia gas at low concentrations (ppb level) while at room temperature, without fouling due to humidity. The goal for the research is to produce a reliable, highly sensitive and selective ammonia gas sensor for field applications.

A5.18

Single aperture functionalization for bio-organism sensing applications.

Joakim Nilsson, Louisa J. Hope-Weeks and Sonia E. Letant; Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, California.

Chemically functionalized apertures with large aspect ratios constitute a platform of choice for bio-organism sensing. We fabricated apertures on pre-patterned silicon platforms with aspect ratios >10:1 using focused ion beam (FIB) drilling, followed by dry/wet oxidation. Localized DNA functionalization of the nanopores was then achieved by self-assembled monolayer chemistry combined with a silicon nitride mask. Ionic flow measurements recorded through single nanopores at each stage of the device preparation allowed to demonstrate the open nature of the channels and to follow the aperture functionalization

process step by step. The chemical selectivity of the DNA-functionalized devices will be investigated by measuring the duration and amplitude of the ion current blockade generated by single DNA-functionalized beads electrophoretically driven through the apertures. Future applications include the selective detection of bacteria and viruses. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

A5.19

Chemical Vapor Depositions of Single-Walled Carbon Nanotube Thin Films and its Sensing Applications in Aqueous Solutions. Qiang Fu, Lei An, Chenguang Lu and Jie Liu; Chemistry, Duke Univ, Durham, North Carolina.

Since the discovery of the carbon nanotube in 1991 by Iijima, carbon nanotubes have been intensively studied in chemistry, physics and materials science. Single-walled carbon nanotubes (SWNTs) are formed by a single layer of graphene and can be either metallic semiconducting or metallic depending on the helicity and diameter. Field effect transistors fabricated from semiconducting SWNTs have shown high mobility and high sensitivity to absorbates. Such characteristics make SWNTs FETs ideal candidates for sensor applications. However, at current stage there are no methods to selectively synthesize semiconducting SWNTs, and thus fabricating sensor based on SWNTs FET is time and labor consuming. However, this hurdle can be circumvented by utilizing SWNTs thin film FETs using the ensemble properties of large number of SWNTs in the film. Our result is going to include high density SWNTs directly synthesized on surface with catalyst delivered by diblock copolymer, device fabrications and characterizations of FETs based on thin film and sensing applications of SWNT thin film devices in aqueous solutions.

A5.20

Design and Assembly of Iron Oxide and Composite Nanoparticles for Chemical Sensors. Lingyan Wang, Li Han, Xiajing Shi, Lisa Cousineau, Wilbur Kung, Jin Luo, Susan Lu and Chuan-Jian Zhong; Chemistry, SUNY-Binghamton, Binghamton, New York.

Iron oxide and composite core-shell nanostructured materials provide intriguing opportunities for designing new chemical/biological sensors with high sensitivity and selectivity because of its good resistance. In this paper, we will describe recent results of an investigation of the synthesis of iron oxide nanoparticles and their composite nanoparticles. By controlling the reaction temperatures and manipulating the capping agent properties and solution compositions, we have prepared gamma-Fe₂O₃ and Fe₃O₄ nanoparticles in 2-20 nm size range with different sizes, shapes, and core-shell compositions. The nanoparticles are characterized using TEM, ED, DCP, TGA, XPS, XRD, FTIR, and SQUID techniques. Molecularly-mediated nanoparticle assemblies of the nanostructures have been tested for characterizing their sensory properties in detecting toxic gases and volatile organic compounds. Preliminary results will be discussed, along with their pattern recognition in designing advanced sensing nanomaterials.

A5.21

Long-Term Stability and Characteristics of Polyaniline Sensor Coated with Poly(vinylidene fluoride) for VOCs. Joonbo Yu¹, Jungsuk Kim², Sungok Sohn¹ and Jeungsoo Huh¹; ¹Material Science and Metallurgy, Daegu, South Korea; ²Nano-science and Technology, Daegu, South Korea.

The problem of polyaniline(PANI) sensors has been poor chemical and mechanical stability under atmosphere condition. In this study, the polyaniline sensor coated with polyvinylidene fluoride(PVF2) was employed for improvement of chemical characteristics. The morphology of PVF2 coated PANi later was appeared to be smooth and transparent at 15%concentration of coating solution. The resistance of PVF2 coated PANi was kept constant and had a good stability at long-term exposure of humidity. The sensitivity of PANi sensors was maintained for two months, while coated PANi sensor was maintained over four months. The coated PANi sensors was exposed to various VOC gases, including methanol, ethanol, toluene and benzene, to investigated the variation of sensitivity. The linearity between sensitivity and gas concentration was good in the range of 100ppm to 1000ppm. The highest sensitivity was detected from ethanol gas.

A5.22

Effects of Various Annealing Temperature on Carbon Nanotubes for N₂ Detection. Bohr-Ran Huang, Chien-Sheng Huang, Yong-Huang Chang, Chih-Fu Hsieh, Chia-Ching Wu and Min-Chao Chen; Electronic Engineering Department, National Yunlin University of Science and Technology, Touliu, Yunlin, Taiwan.

The vertically aligned carbon nanotubes (CNTs) deposited by microwave plasma-enhanced chemical vapor deposition (MPCVD) were utilized as resistive gas sensors. The carbon nanotubes were annealed between 200 to 800 degrees centigrade under N₂ flow (500 sccm) for 15 minute, respectively. After that, the carbon nanotubes were exposed to an N₂ filling and pumping environment. Upon exposure to N₂ the electrical resistance of vertically aligned carbon nanotubes was found to increase. It was found that the N₂ absorption of unannealed carbon nanotubes was reversible, whereas which of annealed ones was not. However, the sensitivity of the N₂ absorption on carbon nanotubes was improved after annealing. From the Raman spectra, the ID/IG ratio of carbon nanotubes also decreased after annealing, indicating that more graphenes were formed by the annealing process. Furthermore, from X-ray photoelectron spectroscopy (XPS), it was observed that the ratio of the oxygen to carbon (O/C) signal intensity increased from 0.15 to 1.88 as the annealing temperature increased. As a consequence, it was suggested that the surface of carbon nanotubes was oxygenated and the absorption of N₂ changed from physisorption to chemisorption.

A5.23

Piezoresistive characteristics of a microcantilever integrated with boron-doped polysilicon resistor for biosensors.

Kwang-Ho Na¹, Jae Young Kim¹, Chi Jung Kang² and Yong-Sang Kim¹; ¹Electrical Engineering, Myongji University, Yongin, South Korea; ²Physics, Myongji University, Yongin, South Korea.

The microcantilever designed for atomic force microscopy (AFM) was recently used for another purpose, namely, to investigate the change in environment, such as temperature, humidity, pH, and electric potential. Its widespread availability has resulted in renewed interest in using surface stress-based biosensors as means of detecting the deflection caused by the adsorbed biomolecule. The amount of bending of the cantilever beam can be detected by widely used optical detection method. There are, however, several disadvantages. First, they require external devices for deflection measurements such as laser assembly. In addition, the alignment and calibration of these external elements are necessary. Furthermore, the overall dimensions and power requirements for such detection systems can exceed the requirements of field for biochemical detection purpose. These disadvantages can be avoided by integrating the detection elements or devices into the cantilever. One method is to put the piezoresistor in the cantilever. When a piezoresistive material such as polysilicon is strained, its electrical conductivity is changed. We investigated piezoresistive characteristics of microcantilever based biosensor. The 300nm-thick LPCVD polysilicon was used as a piezoresistor with boron implantation (4E14cm⁻² of dose and 30 keV of energy) and was encapsulated with LPCVD silicon nitride film. The cantilever bends due to the difference of the surface stress caused by the formation of a glutaraldehyde/cystamine dyhydrochloride bilayer on the gold-coated microcantilever. In order to measure the change of the resistance, constant voltage source was supplied and current was monitored. The fluid cell for liquid flow was fabricated using PDMS and glass. The liquid flow was driven by gravity and the flow rate of 12 14?l/min was kept constant during the whole measurement. The cystamine (50mM) terminated with thiol was covalently immobilized on the gold-coated side of the cantilever and glutaraldehyde(2%) that would be bonded with amine group in the cystamine was injected subsequently. This process was characterized by measuring the deflection of the cantilever in real time monitoring. The resistance change of more than 500 ohms was observed after injection of cystamine and glutaraldehyde, which is the same result as that of optical measurement. The piezoresistive characteristics are investigated as functions of various biomolecules and boron implant dose concentrations from 1E13 cm⁻² to 1E16 cm⁻².

A5.24

Oxygen effect on the surface conductivity of n-type sulfur-doped diamond film in aqueous solutions.

Ileana Gonzalez-Gonzalez¹, Donald Al. Tryk¹, Carlos Raul Cabrera¹, Geraldo Morell² and Joel De Jesus²; ¹Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico; ²Physics, University of Puerto Rico, Rio Piedras, Puerto Rico.

Recently there has been much interest in the phenomenon of surface conductivity of diamond films and the effect of various adsorbates on this conductivity. Specifically, it has been found that oxidizing conditions tend to increase the surface conductivity of boron-doped diamond films and reducing conditions tend to decrease the conductivity. An example of an oxidizing condition is a low pH aqueous solution. Another example an oxygen saturated solution. One possible mechanism for the increased conductivity that results from the presence of an oxidant involves the transfer of electrons from the bulk of the p-type boron doped diamond to the adsorbate, which effectively increases the number of p-type charge carriers (holes). (1,2) This increase in conductivity can be used to as a way to sense the presence of an oxidant such as oxygen. Thus far, this phenomenon has only been reported for p-type diamond films.(3) Recently, we have

found in our laboratory that a similar phenomenon also occurs on n-type diamond films, such as sulfur-doped films. Sulfur is a deep donor in diamond.(4, 5) In this case, however when the electron is transferred from the diamond to the oxidant, the number of n-type charge carriers (electrons) is decreased, and the surface conductivity decreases. This also results in decreases in the currents for oxygen evolution and hydrogen evolution from an aqueous solution. We have used the latter observation as a means of measuring the concentration of oxygen dissolved in aqueous solutions. There is a rough correlation between the electrochemical behavior and the sulfur doping level for a series of nanocrystalline films prepared as described previously.(6) In particular for high doping levels, the decrease in current upon exposure of the solution to air is small, whereas for low doping levels the relative decrease is large. (1) J. Ristein, F. Maier, M. Riedel, M. Stammer, and L. Ley, *Diamond Rel. Mater.*, 10, 416 (2001). (2) D. Takeuchi, S. Yamanaka, and H. Okushi, *Diamond Rel. Mater.*, 11, 355 (2002). (3) V. Chakrapani, S. C. Eaton, and J. C. Angus, *Extended Abstracts, Diamond Materials VIII, Spring Meeting of the Electrochemical Society (Paris), The Electrochemical Society, Pennington, N.J., U.S.A. (2003)*. (4) H. Titus, V. Albu, A. B. Anderson, and J. C. Angus, *J. Electrochem. Soc.*, 149, E143 (2002). (5) E. Gheeraert, N. Casanova, A. Tajani, A. Deneuville, E. Bustarret, J. A. Garrido, C. E. Nebel, and M. Stutzmann, *Diamond Rel. Mater.*, 11, 289 (2002). (6) A. Gonzalez-Berros, D. Huang, N. M. Medina-Emmanueli, K. E. Kristian, O. O. Ortiz, J. A. Gonzalez, J. De Jesus, I. M. Vargas, B. R. Weiner, and G. Morell, *Diamond Rel. Mater.*, 13, 221(2004).

A5.25

Highly Oriented Thin Film Composites of V_2O_5 and V_6O_{13} , Grown by MOCVD for Gas Sensing. M.B. Sahana and S.A. Shivashankar; Indian Institute of Science, Bangalore, Karnataka, India.

The vanadium oxide system is interesting because of diverse physical properties observed in apparently similar phases. For example, while vanadium pentoxide is a wide band gap semiconductor, V_6O_{13} , which has a very similar structure, is a metal at room temperature. It may be expected from the V-O binary phase diagram that the free energy of V_6O_{13} is likely to be close to that of V_2O_5 . Further, along the a-b plane, both the structures have very similar polyhedral connectivity and a similar two-dimensional repeat unit. This suggests a rather facile inter-convertibility between V_2O_5 and V_6O_{13} through oxidation/reduction in suitably oriented thin films. Thus, the electrical conductivity of films comprised of V_2O_5 or V_6O_{13} may be expected to change sharply due to easy conversion between the two phases, through adsorption, chemical reaction, and desorption mechanisms. For this reason, films comprised of (001)-oriented V_2O_5 or V_6O_{13} are candidate materials for gas sensing applications. We have shown that, through metalorganic chemical vapor deposition (MOCVD) that employs a β -diketonate precursor, it is possible to grow strongly oriented vanadium oxide films on smooth amorphous substrates, exploiting crystal structure anisotropy. Such growth takes advantage of the tendency for surface energy minimization, which promotes oriented growth on smooth amorphous substrates. Specifically, the a-b planes of both V_2O_5 and V_6O_{13} are made up of a network of corner sharing zig-zag strings consisting of edge-shared polyhedra, forming closely packed dense planes. Therefore, thin films of V_2O_5 and V_6O_{13} grown on fused quartz by MOCVD (using vanadyl acetylacetonate as the precursor) may be expected to grow with the (001) orientation, suitable for sensing devices. Such films were characterized by XRD, SEM, TEM, RBS, and UV-visible spectrophotometry. The dependence of degree of (001) orientation and the composition of the films on growth temperature will be discussed. Further, the suitability of strongly oriented films of V_2O_5 and V_6O_{13} grown on fused quartz by MOCVD in sensing gases such as oxygen has been examined. The results of these experiments will be presented.

A5.26

In2O3 Nanowires as Protein Sensors. Tao Tang, Chao Li, Daihua Zhang and Chongwu Zhou; Electrical Engineering Electrophysics, University of Southern California, Los Angeles, California.

Low-density lipoprotein (LDL) is the major cholesterol transport agent in human plasma and it is suggested to directly relate to some cardiovascular diseases. An analysis of LDL, especially its oxidized form (ox-LDL), is a widely utilized diagnostic technique for these diseases. We have developed sensors for both LDL and ox-LDL based on single-crystalline In2O3 nanowires. These nanowires were first utilized to construct field effect transistors, and antibodies to ox-LDL or n-LDL were subsequently immobilized on the nanowire surface. Upon exposure to n-LDL or ox-LDL, the devices with matched antibody and antigen all showed a large increase in conductance along with a shift in the threshold voltage. In contrast, the devices with mismatched antibody and antigen showed much smaller change in both the conductance and the threshold voltage. Our work demonstrates the potential of identifying biomedical species with

similar structures in a complex environment.

A5.27

0V Bias Neutron Detection of Semiconducting Boron-Carbon Films. Ellen Day¹, M. J. Diaz² and S. Adenwalla²; ¹Mechanical Engineering and Center for Materials Research and Analysis, University of Nebraska, Lincoln, Lincoln, Nebraska; ²Physics and Astronomy and Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska.

The development of boron rich solid state neutron detectors has recently become a reality due to the development of a plasma enhanced chemical vapor deposition (PECVD) method that results in the growth of semiconducting boron carbide films [1]. Boron-carbide/silicon heterojunction diodes have been fabricated and shown to be real time, solid-state neutron detectors [2, 3]. Earlier devices demonstrated neutron detection but required an external bias. Initial experiments in self-biasing with these devices indicate that self-biased heterojunction diodes are also capable of neutron detection, the advantage of which is a lower noise peak. The integrated counts increase with increasing incident neutron flux. Comparisons of externally biased and self biased pulse height spectra reveal the dependence of the spectra on charge collection efficiencies. The possibility of 0V biased neutron detection and production of charge pulses provides a novel way of producing electrical power from incident thermal neutrons. The efficiency of this process will be discussed. This work is partially funded by the State of Nebraska and U.S. Department of Energy National Nuclear Security Administration Office of Nonproliferation Research and Engineering [NA-22] through Pacific Northwest National Laboratory and the Office of Naval Research grant N00014-04-1-0605. [1] Lee, S; Mazurowski, J; Ramsmeier, G; Dowben, P; *Journal of Applied Physics* 72(10): 4925-4933 (1992) [2] Adenwalla, S; Welsch, P; Harken A; Brand, JI; Sezer, A; Robertson, BW; *Applied Physics Letters* 79(26): 4357-4359 (2001) [3] Robertson, BW; Adenwalla, S; Harken A; Welsch, P; Brand, JI; Dowben, PA; Claassen, JP; *Applied Physics Letters* 80(19): 3644-3646 (2000)

A5.28

Fabrication and Testing of Printed Organic Electronic Devices made using High Volume Printing Processes. Yu Xia², Anupama Karwa², Franz Sigg³, Daniel M. Clark⁴, Kalathur Santhanam² and Bruce Kahn^{1,2}; ¹Imaging and Photographic Technology, Rochester Institute of Technology, Rochester, New York; ²Materials Science and Engineering, Rochester Institute of Technology, Unite State, Rochester, New York; ³School of Printing Media, Rochester Institute of Technology, Rochester, New York; ⁴Printing Application Laboratory, Rochester Institute of Technology, Rochester, New York.

Printing is a promising technique to fabricate organic electronic devices such as Organic Light Emitting Diodes (OLEDs), Thin Film Transistors (TFTs), solar cells and sensors. A number of devices fabricated by ink-jet or screen printing have been reported which showed good performance. In this investigation, we report the preparation of such devices using high volume printing techniques (rotary letterpress, flexography, and offset lithography), which are necessary for low cost and batch production. Inks based on organic and inorganic materials have been prepared which have the properties of insulators, sensors, semiconductors and conductors. Multiple impression printing was used to create sequential functional layers in order to obtain all printed organic electronic devices. Surface morphology and interface structure was studied using microscopy and profilometry. Device characteristics were measured and compared with traditional spin-coated organic devices.

A5.29

Printable Electronics: Patterning of Conductive Materials for Novel Applications. Anupama Karwa², Yu Xia², Franz Sigg³, Daniel M. Clark⁵, Thomas W. Smith⁴ and Bruce Kahn^{1,2}; ¹Imaging and Photographic Technology, Rochester Institute of Technology, Rochester, New York; ²Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York; ³School of Print Media, Rochester Institute of Technology, Rochester, New York; ⁴Department of Chemistry, Rochester Institute of Technology, Rochester, New York; ⁵Printing Application Laboratory, Rochester Institute of Technology, Rochester, New York.

The convergence of fields like materials science, printing, and electronics promises to offer low cost, high volume devices such as transistors, solar cells, RFID tags and many other applications. Although a number of emerging 'soft lithographic' techniques have been used to make these devices, soft lithography is slow, and can only be used to produce a limited number of devices. Here we investigate the formulation of inks for high volume printing processes using electrically functional polymers. The inks have been designed to obtain uniform coatings while maintaining the appropriate electrical

characteristics. In this work, the high volume printing processes rotary letterpress, flexography and offset lithography have been investigated. Various parameters like type of substrate, inking time and speed, printing pressure, printing force, and ink formulation have been studied. The prints were characterized to examine surface morphology, adjacent layer interfaces, directional printing effects, and electrical and physical properties.

A5.30

Selectivity Enhancement of Tin Oxide Gas Sensor. Brian P. Mosher and Taofang Zeng; North Carolina State University, Raleigh, North Carolina.

Semiconductor chemical gas sensors have wide applications and are presently a commercial product. The sensors measure the change of electrical resistance upon exposure to certain gases. The scale of change of the resistance distinguishes the gases and their concentration. Selectivity is the key to reliable and multi-functional gas sensors. Recently new approaches have been proposed to improve the selectivity of tin oxide based gas sensors through modifying the compositions of the sensing materials, modulating the operational temperature, and changing the geometrical structure of the sensors. We select copper oxide and cerium oxide as the dopants to enhance the selectivity for detecting NO, CO and CH₄. The oxide and the sensor are prepared using a sol-gel process and screen printing technique. Tests are also performed at different operating temperatures.

A5.31

Intrinsically Safe Intelligent sensors/Transducers based on Ceramic based thin film sensor for Hazardous areas. Sudhir Kumar, CMRI, Dhanbad, Jharkhand, India.

In the era of Electronics & communication technology which rules almost all process methodology of a processing industry supported by quick and efficient communication facility for ameliorating production and productivity of the industry, Sensors/Transducers remain core of the processing. Especially for hazardous industries e.g. Petro-chemical, Pharmaceutical, Explosive, Oil and Natural Gas, Mining Industries etc. where toxic and combustible gases prevail reliable, sensitive and fast response sensors with associated electronic control circuits build a potential system for monitoring and control of environmental parameters for smooth workings and safety of man and machinery. With the advent of Thin /Thick Films, Nano-technology and sensors based on Polymer technology, nos. of Physico-mechanical, electro-optic, Electrical Chemical sensors/actuators have been designed which have edge over resistive and semi-conductor sensors in term of their better and reliable performances. Author in this paper describes advancement in sensors based on development of thin film, Nano-technology and Polymer technology. Author in this paper also briefs ceramic based thin film intrinsically safe combustible and toxic gas monitor devices designed in laboratory for their uses in hazardous and tough environmental areas. The device incorporates in itself self-corrective intelligent circuits to compensate thermal runaway for error free and accurate continuous monitoring of gas percentage. Self-diagnostic circuit also incorporates in the system as a precursor (Forewarning) to depict the status of intrinsically safe power supply. Based on the studies and experiments carried out in laboratory, the author finally categorizes advanced thin film and polymer materials which could assist in developing different sensors for suitable measuring parameters.

SESSION A6: Bio-Chemical Sensors
Chairs: Duk-Dong Lee and Satyajit Shukla
Wednesday Morning, December 1, 2004
Back Bay D (Sheraton)

8:30 AM *A6.1

Carbon Nanotube Based Bio and Chemical Sensors. M. Meyyappan, NASA Ames Research Center, Moffett Field, California.

Carbon nanotubes (CNTs) exhibit unique electrical and extraordinary mechanical properties and therefore have been the subject of investigation for various applications. Here we focus on bio and chemical sensor fabrication and characterization. The biosensor uses vertically aligned, individual, freestanding multiwalled carbon nanostructures to fabricate nanoelectrodes. Functionalization of the nanotube ends with probe molecules, sensing and electrochemical amplification of the signal have been demonstrated and will be discussed in detail in this talk. The second application involves an interdigitated electrode based chemical sensor wherein nanotubes form the sensor material. Exposure to gases like NO₂, ammonia, and a variety of organic vapors produces reproducible changes in nanotube conductivity. The fabrication and operation of chemical sensor based on conductivity change will be discussed. The author acknowledges

contributions from Jun Li, Alan Cassell, and Jing Li.

9:00 AM A6.2

Encapsulation of Urease in Molybdenum Trioxide Sol-Gel. Prashant Kumar Jha and Pelagia Irene Gouma; Department of Material Science, State University of New York at Stony Brook, Stony Brook, New York.

Molybdenum trioxide Sol-Gel matrices were tested for their ability to host biomaterials in their structures without adversely affecting the activity of the encapsulated biomolecules. The sol-gel composites were prepared at room temperature; the urease was added during the hydrolysis step to ensure proper encapsulation in the pore structure of the sol. Phosphate buffer solution was added during this stage to maintain the pH value of the sol in the bio-compatible range (pH6-9). The activity of incorporated urease was tested by exposing composite sol-gel material to standard urea test solutions and measuring the amount of gaseous ammonia (released by the reaction of urea with water in the presence of urease) using an ammonia electrode. The concentration of urea solutions ranged from 10mM to 1mM and the concentration of released ammonia that was measured was in the range of 200-400ppm. Effects of ageing, drying and temperature on the stability of the biocomposite material were also studied. Microstructural analysis was done by means of transmission and scanning electron microscope. In the summary it was found that urease retained its activity inside molybdenum trioxide sol-gel. These hybrid nanoporous composites are useful in the field of biosensors and fuel cells.

9:15 AM A6.3

Towards Tethering Ion Channels Embedded in Synthetic Bilayers Over Microelectronic Devices. Randy S. Duran¹, Peter Anderson², Jun Zhang¹, Ingo Koeper³, Wolfgang Knoll³, Ananth Dodabalapur⁴, Dan Fine⁴, Fan Ren⁵, Stephen Pearton⁶, Andreas Offenhauser⁷ and Sven Ingebrandt⁷; ¹Chemistry, Univ of Florida, Gainesville, Florida; ²Whitney Laboratory, University of Florida, St. Augustine, Florida; ³Max Planck Institute for Polymer Research, Mainz, Germany; ⁴Electrical Engineering, University of Texas, Austin, Texas; ⁵Chemical Engineering, University of Florida, Gainesville, Florida; ⁶Materials Science, University of Florida, Gainesville, Florida; ⁷Julich Research Center, Julich, Germany.

We have prepared ion channel and extremophile lipid assemblies with a view towards using them in tethered bilayers over microelectronic devices for eventual biosensor applications. Since picoamp currents of potassium ions through a high capacitance organic in an immersed aqueous environment must be measured, a number of surface engineering issues arise. We discuss progress on systems based on Au, Si, GaN, and other device surfaces. Performance of these devices in HEMT, ISFET, JFET and other architectures will be introduced.

9:30 AM A6.4

The label-free DNA detection using diamond FET based on its molecular charge. Yusuke Nakamura¹, Song Kwang-Soup¹, Zhang Guojun^{1,2}, Yang Jung-Hoon¹, Kei Furukawa¹, Shota Kawamura¹, Yoshinori Sasaki¹, Munenori Degawa¹, Hitoshi Umezawa¹, Iwao Ohdomari^{1,2} and Hiroshi Kawarada¹; ¹School of Science & Engineering, Waseda University, Tokyo, Japan; ²COE, Tokyo, Japan.

Recently, there is a need for sensitive detection of biological molecules such as protein and DNA in order to early detection and rapid cure of diseases with advance in medical technology. From the point of biochemical applications, diamond has many advantages such as wide potential window, low background currents, chemical stability and biocompatibility. It is expected that diamond can be applied to electrochemical electrode, chemical sensor, and biosensor. In our previous study, we have fabricated enzyme biosensors immobilizing urease and glucose oxidase on channel surface of electrolyte-solution-gate field-effect-transistors (SGFETs) using p-type surface conductive layer of hydrogen-terminated diamond. Here, we introduce DNA sensors using SGFETs for real time detection of hybridization. We immobilized probe DNA on the glutaraldehyde-treated channel surface of SGFETs and delivered target DNA sample solution at room temperature. Gate potential of SGFETs decreases following addition of complementary target DNA (cDNA) sample solution. It is thought that hole concentration induced in channel of SGFETs increased by doubled volume of phosphate group with negative charge for DNA-DNA hybridization. However, gate potential hardly changes at all following addition of a noncomplementary target DNA (ncDNA) sample solution. A relationship between gate potential-change and cDNA concentration (10nM, 100nM, 1μM) shows amount of potential-change gets smaller with decreasing cDNA concentration, so it can be said that cDNA can effectively and selectively detect concentrations as low as ca. 10nM with the devices used in this study without labeling and in real-time. This DNA detection method is direct, label-free DNA detection with

good selectivity, and could provide a way of highly sensitive detection by miniaturization of device scale. Furthermore, it has a potential for wide clinical application utilizing biocompatibility of diamond.

9:45 AM A6.5

Chemical Modification of Gallium Nitride Based BioFETs for Biomolecular Detection. Kendra Michele McCoy^{1,2}, J. C. Smith², S. J. Pearton³ and L. J. Whitman²; ¹Department of Chemistry, University of Florida, Gainesville, Florida; ²Chemistry Division, Naval Research Laboratory, Washington, District of Columbia; ³Department of Materials Science and Engineering, University of Florida, Gainesville, Florida.

Biologically modified field effect transistors (BioFETs) offer the possibility for label-free, real-time detection of biologically active molecules for a myriad of applications. In order for a FET device to perform such functions, it must satisfy three major criteria: the bioFET must be sensitive to the biological interactions being probed; it must be stable in the biological environment; and the surface of the bioFET must be functionalized for biomolecular recognition. BioFETs based on gallium nitride (GaN) could potentially satisfy all of these requirements. As a first step to achieving this goal, we are developing a scheme to passivate GaN surfaces with self-assembled monolayers and polymers to create surfaces amenable to subsequent functionalization with biological probes such as single stranded DNA and antibodies. We are evaluating a number of methods based on amine and thiol chemistry, and characterizing the resulting surfaces by x-ray photoelectron spectroscopy and electrochemical techniques. For example, we have found that amine terminated SAMs can react with gallium nitride surfaces, and these SAMs can be used to build passivation layers that can probe the hybridization of DNA. The resulting chemical and electrical properties of the surface layers that are created will be discussed.

10:30 AM *A6.6

Nanoscale Silicon Optical Biosensors. Philippe Fauchet, B. L. Miller, H. Ouyang and L. A. DeLouise; Center for Future Health, University of Rochester, Rochester, New York.

This presentation will review progress in the development of practical nanoscale silicon optical biosensors at the Center for Future Health. The biosensing platform consists of photonic bandgap (PBG) structures made of microporous, mesoporous, or macroporous silicon. The optical properties of the PBG structures, which are controlled by the refractive index inside the pores or air holes, change upon binding of the desired target inside the pores. These changes can readily be measured and quantified by reflectance, transmittance, or photoluminescence measurements. The design of sensitive structures and significant issues in materials and optical science will be discussed in detail. The performance of the devices will be illustrated by examining several biosensing examples, ranging from health monitoring and food safety to biowarfare agent detection.

11:00 AM A6.7

Selectivity Tuning of Macroporous Silicon Chemical and Biological Sensors. Karl D. Hirschman^{1,2}, Deoram Persaud², Vimilan Rajalingam², Jeffrey Clarkson¹, Marie Archer³ and Philippe M. Fauchet³; ¹Microelectronic Engineering, Rochester Institute of Technology, Rochester, New York; ²Materials Science and Engineering, Rochester Institute of Technology, Rochester, New York; ³Electrical and Computer Engineering, University of Rochester, Rochester, New York.

A new class of silicon-based chemical and biological sensors that offer an electrical response to a variety of substances is described. The devices utilize silicon sensing membranes with deep trench structures formed to depths up to 100 microns, fabricated by electrochemical etching which transforms the silicon into macroporous silicon (M-PSi). The sensors have demonstrated the ability to detect the presence of certain chemical and biological materials. Although the principle of operation of the devices is fairly complex, the transduction mechanisms can be compared to chemiresistors and chemically sensitive field-effect transistors (chemFETs). The electrical responses that have shown the most sensitivity are AC conductance and capacitance. Previous work has demonstrated that upon exposure to organic solvents (i.e. ethanol, acetone, benzene) the devices exhibit a characteristic impedance signature. The devices have also shown the ability to detect the hybridization of complementary DNA. By placing appropriate probe materials within the detection region of the device, the range of detectable substances can be expanded while tuning the selectivity. The incorporation of polymers and metals that have demonstrated sensitivity to low ambient levels of contaminants is the current focus of this investigation. It is expected that these materials will provide an electrically detectable signal upon exposure to a specific target substance; either through a change in permittivity, work function or charge state which will alter the impedance characteristic of the device.

11:15 AM A6.8

Covalently Modified Diamond and Silicon Surfaces: Resistance to Non-Specific Protein Adsorption and Optimization for Biosensing. Tami Lasseter Clare¹, Brian H. Clare^{2,1}, Nicholas L. Abbott² and Robert J. Hamers¹; ¹Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin; ²Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin.

Oligoethylene glycol monolayers on gold and SiO₂ surfaces have been used to resist the non-specific adsorption of proteins and cells. This ability to resist biofouling is important for the design of biocompatible coatings (e.g. diamond and diamond-like carbon) for implants and for biosensors capable of detecting analytes in complex protein mixtures. Covalently-modified surfaces of silicon and of diamond thin films are now emerging as useful materials for the direct electrical detection of biomolecules. We describe the direct covalent functionalization of silicon and of diamond with a variety of short ethyleneglycol (EG) oligomers via photochemical reaction of the hydrogen-terminated surfaces with terminal vinyl groups of the oligomers. Our results show that the functionalized surfaces resist the non-specific adsorption of avidin, BSA, casein, and fibrinogen by greater than 90% compared with amino-terminated monolayers which adsorb approximately 0.5 pmol of avidin per cm² as determined by fluorescence wash-off measurements. We also demonstrate the preparation of mixed monolayers on silicon and diamond, characterize these layers using XPS, and apply these surfaces to optimize the ratio of specific to non-specific binding in a model protein sensing assay.

11:30 AM A6.9

Electronic Detection of Nucleic Acid Molecules with a Field-Effect Transistor. Sven Ingebrandt, Yin-Hua Han, Oleksandr Belinsky and Andreas Offenhausser; Inst. Thin Films & Interfaces (ISG-2), Forschungszentrum Julich, Julich, Germany.

Commonly used, label-free techniques for the detection of DNA are based on the direct measurement of the intrinsic electrical charge of DNA or on capacitance and impedance changes at the surface. Most of the sensors are using cyclic voltammetry, pulse voltammetry or chronopotentiometry together with redox-active indicators. Recently the detection limit of field-effect sensors was enhanced such that single base mismatches in 12-mer oligonucleotides can be detected. We developed a 16-channel field-effect transistor (FET) recording system which were fabricated following a protocol previously described. A passivation sandwich layer of silicon nitride and oxide and a gate oxide thickness of 10 nm (SiO₂) for the FET sensor surface was chosen. This surface was found to be stable for repeated use of the devices. For the measurements with DNA a flow-through cell for liquid handling was used. For the attachment of DNA or polyelectrolytes the FET surfaces were silanized with 3-Aminopropyl-triethoxysilane (APTES). All measurements were performed in 10mM TRIS (hydroxymethyl) aminomethane buffer solution with a sodium chloride concentration of 1 mM at pH 7. We are detecting DNA at the surface by measuring the surface potential at the gate. DNA carries one negative charge per base at the phosphate groups of the backbone. The accumulation of negative charges at the gate oxide causes a shift in the flatband voltage of the transistor, which results in a voltage drop of the output signal in a time-dependent measurement. Therefore the immobilization and hybridization can be detected as negative voltage drops in the output signal, while attachment of positively charged polyelectrolytes (polyallylamine hydrochloride PAH) results in a positive signal. The detection principle of the system was confirmed in many test measurements using differently charged polyelectrolytes. A strong dependence of the signal amplitude on the concentration of sodium chloride in the buffer solution was found. We determined a maximum sensitivity of our FET system at 1mM sodium chloride concentration. At this un-usually low buffer concentration the electrical shielding of the DNA charge is weaker, which results in a stronger FET signal. The signal amplitude for the hybridization events is strongly dependent on the change of surface charge, which is linearly dependent on the density of DNA strands attached to the transistor gate. In an additional experiment we measured the surface coverage of the immobilized DNA strands on our substrates using radioactive labeled DNA. Because of the small size of the FET gates just about 10.000 DNA strands are required to give a large enough signal.

11:45 AM A6.10

Biosensors Based on Organic Thin Film Transistors. Jeff Mabeck¹, Zheng-Tao Zhu¹, Nate Cady³, Carl Batt², Joel Tabb⁴ and George Malliaras¹; ¹Materials Science and Engineering, Cornell University, Ithaca, New York; ²Food Science, Cornell University, Ithaca, New York; ³Microbiology, Cornell University, Ithaca, New York; ⁴Agave BioSystems, Ithaca, New York.

Chemical and biological sensors based on organic thin film transistors (OTFTs) have begun to attract significant interest. Such devices can

be easily and inexpensively fabricated on a variety of substrates, and the organic semiconducting molecules can be chemically synthesized or modified for specific applications. We have previously shown that pentacene OTFTs can be used to make sensitive humidity sensors. In the current work, we demonstrate the applicability of OTFTs for detecting biological species in aqueous environments. Pentacene OTFTs were fabricated on Si substrates with SiO₂ as the gate dielectric, and poly(dimethyl siloxane) (PDMS) microfluidic channels were used to expose the active regions of the transistors to aqueous solutions with a range of ionic strengths and pH as well as buffer solutions containing rat basophilic leukemia (RBL) cells. We will also discuss unusual OTFTs based on the doped conducting polymer poly(ethylenedioxy-thiophene)-polystyrenesulphonate (PEDOT:PSS) and the application of these transistors to DNA and glucose sensing.

SESSION A7: Integration

Chairs: Elisabetta Di Bartolomeo and Hong-Ming Lin
Wednesday Afternoon, December 1, 2004
Back Bay D (Sheraton)

1:30 PM ***A7.1**

Micro Gas Sensors Operating at Room Temperature.

Duk-Dong Lee and Kap-Duk Song; School of Electronic & Electrical Engineering, Kyungpook National University, Daegu, South Korea.

It is well known that most of the semiconductor type gas sensing devices can be operated at the elevated temperature. So the considerable power consumption for the operation of gas sensing device is known to be avoidable. But, until now, the attempts to minimize the power consumption have been made by many researchers. The results of the study on low power gas sensor can be summarized by two categories; one is to miniaturize the device size and the other is to apply some appropriate materials. In the study, low power micro gas sensors operated at room temperature for the detection of NH₃ and NO_x gases are proposed. As candidate material of gas sensor for NH₃ gas detection at room temperature, polyaniline(PANi) synthesized by chemical polarization was selected. And Te(Tellurium) thin film was used for NO_x gas detection at room temperature. By using these sensing materials, micro gas sensors for room temperature operation were prepared and measured the response characteristics for NH₃ and NO_x. In case of PANi sensor, the structure was inverted staggered FET type having advantage of useful one for Lab-On-a-Chip. The operating principle of the sensor is based on the change in work function of PANi film caused by adsorption of gas molecules in air on the film surface. The change in work function was measured indirectly from that in gate voltage of the FET device. The response to various gases (NH₃, CH₄, CO and NO_x) was obtained in gate voltage step mode in R.H. 30%. And in case of Te sensor, the sensing material was thermally evaporated on glass substrate. The thickness and annealing temperature were 500 Å–2000 Å and 100°C–300°C, respectively. And Ti was added to Te film. So the resistance at room temperature is much lower than that of metal oxide semiconductor. The Te-based micro gas sensor exhibited high sensitivity to NO_x and good selectivity against CO and hydro-carbon gases.

2:00 PM **A7.2**

SiGe Thermoelectric Film for Gas Sensor Micro-Devices.

Woosuck Shin, Kazuki Tajima, Yeongsoo Choi, Noriya Izu, Ichiro Matsubara and Norimitsu Murayama; Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology, Nagoya, Japan.

A gas sensor micro-device using both thermoelectric film and catalyst film has been developed on the platform where the operating temperature can be rapidly changed to achieve desired response characteristics, known as a micro-hotplate. SiGe thin films were deposited on the Si₃N₄/SiO₂/Si substrate by RF-sputtering and thermal annealing was carried out to crystallize the as-deposited, amorphous-like SiGe thin films. With increasing the annealing temperature and time, the crystallization of the SiGe thin film progressed, resulting in high carrier mobility and large absolute value of Seebeck coefficient. The micro-heater and the electrodes were patterned by photolithography and lift-off technique. After the back-side etching of Si substrate, the catalyst layer was deposited on the membrane structure. The hydrogen sensitivity of the micro-thermoelectric gas sensors was investigated for various gas concentration and device working temperatures.

2:15 PM **A7.3**

Integration of Microcatalysts on Thin Membrane for Thermoelectric Gas Sensor Devices. Yeongsoo Choi, Woosuck Shin, Kazuki Tajima, Noriya Izu, Ichiro Matsubara and Norimitsu Murayama; Sensor Integrator Group, Advanced Manufacturing Res.Inst.AIST, Nagoya, Japan.

In order to fabricate a highly efficient thermoelectric hydrogen sensor (THS), a dispenser technique was employed. As a catalyst, Pt/alumina paste was dropped on the Si substrate or microdevice. The Pt/alumina catalyst was prepared by the impregnation method using platinum (IV) chloride pentahydrate and commercial alumina. The crystallographic structure, the surface morphology and element analysis of the catalysts were analyzed by the XRD, FE-SEM and SEM-EDX, respectively. The catalytic activities of THS were evaluated by measuring the temperature variations, generated from the oxidation of hydrogen on the catalyst surface, using an infrared camera. When the loading of Pt was 30-40 wt%, the temperature variation showed the highest value. The temperature variation was almost proportional to the hydrogen gas concentration. An interesting result of the temperature variation obtained by the correlation between thermoelectric film and catalysts will be presented in this work.

2:30 PM **A7.4**

The Development and Evaluation of TiO₂ Nanoparticle Films for Conductometric Gas Sensing on MEMS Microhotplate Platforms. Kurt D. Benkstein and Steve Semancik; CSTL, National Institute of Standards and Technology, Gaithersburg, Maryland.

Over the past decade, MEMS microhotplate devices have been developed at the National Institute of Standards and Technology to support semiconductor metal oxide films for use in conductometric gas sensor arrays. In most cases, the materials have been based on compact thin films of SnO₂ or TiO₂ as deposited by single-source precursor chemical vapor deposition. Of particular interest to our group is the enhancement of the sensitivity of the sensors to trace gas species by inducing nanostructured porosity and large internal surface areas in the films. In this presentation, we discuss the development of nanostructured sensor materials based on porous TiO₂ nanoparticle thin films. The preparation and evaluation of pure and niobium-doped TiO₂ nanoparticle films are described. The films on the MEMS microhotplate substrates are evaluated as conductometric gas sensors based on the critical performance elements of sensitivity, stability, speed and selectivity. Rapid control of the sensor operating temperature, an inherent benefit of the microhotplate platform, is employed to improve the performance of the nanoparticle films as sensor materials. The sensor performance of the novel nanoparticle TiO₂ films is compared with that of traditional compact CVD-derived films.

2:45 PM **A7.5**

Low-Cost Integrated Sensors Utilizing Patterned Nano-Structured Titania Arrays Fabricated Using a Simple Process. Zuruzi Abu Samah¹, Andrei Kolmakov², Martin Moskovits² and Noel C. MacDonald^{1,3}; ¹Materials Department, University of California, Santa Barbara, California; ²Chemistry and Biochemistry Department, University of California, Santa Barbara, California; ³Mechanical and Environmental Engineering Department, University of California, Santa Barbara, California.

Chemical sensors are used in a variety of areas such as process control, healthcare, automotive, aerospace and environmental monitoring. Because of their importance, a few critical issues associated with the design and production of high performance chemical sensing devices must be addressed. These include requirements for low cost, miniaturization, and compatibility with large volume manufacturing processes. These issues could be mitigated by developing processes that take advantage of the inherent 'batch-processing' property of microfabrication techniques. In addition, use of microfabrication techniques allows integration of sensing elements with advanced electronics on a single chip. Nanostructured titania (ns-titania) has been used for sensing a variety of gases as well as biological species. However, significant challenges of crack formation, cost issues and incompatibility of current synthesis methods with microelectronics fabrication techniques hinder its implementation on chips. We have developed a simple process that is potentially low-cost and compatible with microelectronics fabrication techniques to implement crack-free ns-titania (anatase) layers by reacting Ti surfaces with aqueous H₂O₂ solution. The formation of single phase nanostructured anatase layers on devices have been investigated using TEM, high resolution SEM, AFM, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). We have also realized sensor devices on Si chips utilizing patterned nanostructured titania arrays as sensing elements. These sensor devices are ultra-sensitive to oxygen and can also sense hydrogen. We shall also present results of investigations to implement ns-titania sensor arrays on flexible, light-weight and robust substrates. These could have implications in development of wearable and low-cost sensors.

3:30 PM ***A7.6**

Integrated and Multiplexed Functional Nanostructures for Bio-Chem Sensors. Vinayak P. Dravid, ¹Materials Science &

The continuing challenges in bio-chem sensing include not only the usual selectivity and sensitivity issues, but economic, ergonomic and power considerations, and efficacy of such sensor systems for integration with low-cost and widely deployable platform (such as MOS), networking and remote-addressability. With the emergence of nanostructures, and the ability to synthesize, manipulate and position such functional nanostructures, there is considerable potential for novel paradigms in sensor materials, signal transduction/detection schemes and integrated systems. Among several approaches at Northwestern, our research is geared towards new and optimized sensor elements for toxic gas sensing as well as novel electronic signal transduction/detection mechanisms for bio-chem binding events. Specifically, the presentation will cover two disparate but interrelated aspects of emerging bio-chem sensor systems: (i) site- and shape-specific dip-pen nanopatterning (DPN) of inorganic sensor elements, and (ii) embedded MOSFET in microcantilevers. We use DPN as an enabling approach to position sensor elements in-between patterned electrode array for conductivity-based detection. On one front, we use sol-gel inks for DPN which allow for multiplexing of composition of sensor elements, such as doped semiconducting oxides such as SnO₂, ZnO, TiO₂ etc.. The small size and mesoporous microstructure of such miniature sensor elements exhibit high sensitivity to gas exposure, while composition optimization (through DPN combinatorial array) provides improved selectivity for specific gases. By creating compositionally differential sensor elements on a single chip, some sensor elements are more selective for specific gases than others. However, collectively they represent a broad differentially responsive array which has the potential to recognize mixture of gases at high sensitivity and deterministic discrimination. In a second scheme, we use embedded MOSFET in microcantilevers coated with appropriate receptors for specific and selective biomolecular interactions. Here, selective binding in biomolecular interactions (e.g., DNA hybridization, antigen-antibody) leads to microcantilever bending, which changes the drain current across the embedded MOSFET channels, thereby providing an electronic signature amenable to amplification and remote-addressability. The presentation will cover these new approaches to bio-chem sensing and provide examples of toxic gas and biomolecular detections.

4:00 PM A7.7

Preparation and Characterisation of Nanostructured Materials and their Applications in an Electronic Nose. Simonetta Capone, Mauro Epifani, Angiola Forleo, Luca Francioso, Pietro Siciliano and Antonella Maria Taurino; Lecce, CNR Institute for Microelectronics and Microsystems, Lecce, Italy.

Great efforts, in gas sensors scientific research, are indispensable to develop high performance and fully reliable prototypes of metal oxide gas sensors. In particular, advances are needed to limit the effect of lacking selectivity and the relatively large long-term drift. In order to enhance the sensitivity to a particular gas and to improve the long-term stability, a particularly promising approach seems to be the control of the grain size. Basically, the effects of the microstructure, namely, the porosity in the packing of the metal oxide particles, the large surface to volume ratio, the grain size are well recognized parameters which control the electrical conduction properties and the gas sensing mechanism. It has been claimed that sensitivity is increased as grain size is decreased as far as the nanocrystalline range, that seems really a critical limit at which the solids show interesting tunable electronic and physical properties. On the other hand, since the dopants may affect the structural and morphological properties of the films and in turn the gas sensing properties of the material, the structural modification of the films as a function of their composition need to be deeper studied. Moreover, the approach aims at solving the problem of poor selectivity of MOS sensors seems to be the use of an array of different sensors with partially overlapping sensitivity. In fact, it is well known that the Electronic Nose can be used as powerful method to discriminate and recognize complex gas mixtures and hence it finds application in numerous fields like monitoring of air pollution and control of the quality of foods. We applied the sol gel process to the preparation of pure and doped SnO₂ nanostructured thin films. Ni, Pt, Pd, Os, Rh were chosen as doping elements for SnO₂. The morphological and microstructural properties of the as-prepared films have been investigated by means of SEM, XPS and X-ray diffraction. All the samples showed a polycrystalline structure that resulted to be dependent on the presence of the particular doping element. Moreover, the obtained devices have been tested as functional materials in the Electronic Nose. In particular, we show the results related to the sensing properties of the our array to different food aroma (olive oils, grain pesticide, milk, peach). As an example, different olive oils headspace samples were measured in order to test the application of the array in an Electronic Nose for the discrimination among different non-commercial mono-cultivar olive oils. The differently modified sensitive materials showed different

sensing characteristics to the headspace of the olive oil, hence modulating the selectivity of the array. PCA analysis was performed on the array responses and the results showed the capability to discriminate olive oils of different quality.

4:15 PM A7.8

Floating-Gate Ion Sensitive Field Effect-Transistor for Chemical and Biological Sensing. Ben Zhao¹, Tsunehiro Sai², Arifur Rahman¹ and Kalle Levon²; ¹Electrical and Computer Engineering, Polytechnic University, Brooklyn, New York; ²Other Department of Chemical and Biological Science and Engineering, Polytechnic University, Brooklyn, New York.

This paper presents the use of floating-gate Ion Sensitive Field-Effect Transistor (FGISFET) as a real-time chemical and biological sensor. The structure of FGISFET is similar to that of an electrically erasable programmable read-only memory (EEPROM), with an extended floating-gate connected to a metallic structure exposed to the environment. The exposed metallic plate connected to the FG serves as a probe for detecting ionic activities. In an earlier work, Indium Tin Oxide (ITO) was used as ion sensitive electrode for the detection of nerve gases [1], and biological agents [2]. In this work, we propose the integration of various ion-sensitive materials with floating gate to form monolithic chemical or biological sensors. The threshold voltage of FGISFET is determined by the material properties of substrate, gate, and gate-oxide and the amount of interface charges and charges trapped into the floating gate. By applying ion-sensitive chemical and biological materials to the floating gate, the threshold voltage of a FGISFET can be modulated in the presence of selective chemical or biological elements. To demonstrate the feasibility of such sensors, FGISFETs have been fabricated in 2-poly 1.2 μm process technology available through MOSIS [3]. The initial threshold voltage of a typical n-type FGISFET was 2.5V. Preliminary measurements were performed using doped aniline trimer for the detection of ammonium gas. The doped aniline trimer was applied to the metallic exposure of FGISFET resulting in a positive shift in the threshold voltage to 5.3V. The threshold voltage shift reflects the additional positive charges on the channel induced by the doped aniline trimer, which has been applied to the floating-gate. FGISFET was then placed inside the desiccator and exposed to 70ppm of ammonium gas. When the doped aniline trimer interacts with ammonium, dedoping occurs on the trimer thus neutralizing its charge and result in a negative shift in the threshold voltage to 4.2V. Our preliminary measurements have confirmed the basic design and operation of FGISFET and it has the potentials for developing integrated and miniaturizable chemical and biological sensors and sensor arrays. [1] Y. Zhou et al., Anal. Chem. 76,2689-2693(2004) [2] Y. Zhou et al., Biosensors and Bioelectronics, In Press(2004) [3] www.mosis.org

4:30 PM A7.9

High-Temperature SiC MOSFET Gas Sensors. Kevin Matocha, Vinayak Tilak, Peter Sandvik and Jesse Tucker; GE Global Research, Niskayuna, New York.

Combustion exhaust emission regulations are gradually tightening to control the emission of NO_x and particulate matter, both of which degrade surface air quality. These stringent requirements require enhanced control of combustion processes in transportation and power generation applications. In automotive applications in particular, low-cost NO_x sensors are desired which can operate in the hot exhaust gas streams at both the entrance and exhaust of the catalyst system. While zirconia-based NO_x sensors are commercially available, their present high cost limits their feasibility for use in mass-production applications. We are presently investigating the use of wide-bandgap semiconductor technology using silicon carbide (SiC) as the NO_x sensing element in automotive lean-burn diesel applications. We have fabricated and characterized SiC-based MOSFETs as NO gas sensors operating at 500 degrees C. SiC depletion-mode MOSFETs were fabricated using an epitaxially-grown n-type channel layer on a p-type buffer layer. After mesa isolation and field-oxide deposition, thermal oxidation was used to form the gate dielectric. The platinum gate was deposited either by sputtering or by electron-beam evaporation to determine the effect of Pt microstructure on the sensing properties of the device. The Pt microstructure was investigated using high-resolution SEM imaging to examine the grain-boundary density for correlation with the device sensitivity. Ohmic contacts were fabricated, and devices were packaged using high-temperature ceramic materials able to withstand the harsh test environment. SiC MOSFETs with both sputtered and e-beam Pt were characterized for sensitivity to 50-1000 ppm of NO in a background stream of synthetic air. During characterization, the Pt gate electrode was grounded to the source, and the drain voltage was held constant at 8V. The drain current was continually monitored for response to the delivered NO concentration. The addition of NO to the background air flow caused a decrease in the measured drain current of the SiC MOSFET gas sensors. The SiC MOSFET sensitivity was characterized as a function of temperature (300-500C)

and with both sputtered and e-beam deposited Pt gates. A SiC MOSFET with sputtered Pt gate was characterized for NO sensitivity at 500C with the sensitivity to NO described by: $\Delta I_{ds} = -7.2e-6 - 2.5e-6 \sqrt{NO \text{ ppm}} + 4.46e-8 (NO \text{ ppm})$.

4:45 PM **A7.10**

Interdiffusion and Reaction of Pd on Atomically Stepped 6H-SiC Surfaces: Progress toward Thermally Stable High Temperature Gas Sensors. C. D. Stinespring¹, A. A. Woodworth², C. Y. Peng¹, K. Meehan³, M. J. Murdoch-Kitt³ and C. L. Anderson³; ¹Chemical Engineering, West Virginia University, Morgantown, West Virginia; ²Department of Physics, West Virginia University, Morgantown, West Virginia; ³Bradley Department of Electrical and Computer Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

SiC is a robust wide band gap semiconductor suitable for fabricating gas sensors for use in automotive, energy, and aerospace applications environments. The simplest of these devices are Pd Schottky diodes whose electrical characteristics change when gases are absorbed. Extensive research performed elsewhere has shown these sensors are subject to long-term degradation at elevated operational temperatures (e.g., 140 hrs at 698 K). This degradation is due primarily to thermal instability (i.e., interdiffusion and reaction leading to the formation of metal-silicides) at the metal-semiconductor interface. We have performed controlled studies to investigate the impact of improved substrate surface quality on interfacial stability in these devices. In the studies reported here, highly uniform, atomically stepped 6H SiC (0001) surfaces prepared by high temperature hydrogen etching have been used to investigate the Pd-SiC substrate surface interaction. These substrates are free of both the surface and sub-surface damage left behind by the wafer polishing process. The Pd films range in thickness from 0.2 nm to 40 nm and are deposited under ultrahigh vacuum conditions at 323 K. These films are characterized in-situ using Auger electron spectroscopy (AES) both before and after annealing at 943 K. The AES lineshapes provide quantitative information on the chemistry of the reaction products. Ex-situ atomic force microscopy is used to characterize changes in surface morphology. As a basis for direct comparison, equivalent experiments are performed using "standard" 6H-SiC surfaces typical of those used to date in device fabrication and testing studies. For the thick films (40 nm), electrical characteristics have been measured as well. The results show that different transport processes are effective for the stepped and standard surfaces, and these lead to entirely different nanostructures, both laterally and normal to the surface. The origins of these differences may be traced to differences in the initial Pd-SiC surface interaction. For the stepped surfaces, Pd films less than 2 atom layers thick are thermally stable when annealed at 943 K. For films greater than 2 atom layers in thickness, there is a transition to the outward growth of crystalline Pd-silicide when annealed at 943 K. This appears to involve the out-diffusion of Si. For the standard surfaces, Pd reacts from the onset (i.e., films less than two layers), and this process apparently involves Pd in-diffusion. In the presentation, these results will be described in more detail, and their implications for sensor development will be discussed.

SESSION A8: Physical Sensors

Chairs: Maria-Cristina Carotta and Lhadi Merhari
Thursday Morning, December 2, 2004
Back Bay D (Sheraton)

8:30 AM ***A8.1**

Ferroelectric Materials for Sensor Applications. Dragan Damjanovic¹, Marija Kosec², Marc Lethiecq³, Lorena Pardo⁴, Mai PhamThi⁵ and Erling Ringgaard⁶; ¹Ceramics Laboratory, EPFL, Lausanne, Switzerland; ²Institut Jozef Stefan, Ljubljana, Slovenia; ³LUSSI, Université François Rabelais, Tours, France; ⁴ICMM, CSIC, Madrid, Spain; ⁵Ceramics & Packaging Department, Thales Research and Technology, Orsay, France; ⁶Ferroperm Piezoceramics AS, Kvistgard, Denmark.

Ferroelectrics are multifunctional materials which can couple various types of variables, including mechanical/acoustic and electric fields (piezoelectric effect), infrared radiation and electrical properties (pyroelectric effect), and, in some cases, directly or indirectly, magnetic and electric fields (magneto-electric or magneto-elasto-electrical effect). Ferroelectrics are thus widely used or have interesting potential as active materials in different sensor systems. In this paper we shall discuss recent developments in application of ferroelectric materials in form of films, bulk materials and composites for pressure and acoustic sensors, chemical sensors using pyroelectric effect, and magneto-electric sensors. It will be demonstrated how properties of ferroelectric sensors (e.g., charge pressure hysteresis in pressure sensors) can be successfully tailored by doping, and by controlling microstructure, composition and crystal

structure. Recent results obtained in the framework of a European project on high sensitivity piezoceramics for advanced applications are discussed. This work was partly funded by European Commission, through FP5 project PIRAMID, contract No. G5RD -CT-2001-00456

9:00 AM **A8.2**

Pressure Induced Changes in the Conductivity of AlGaN/GaN High Electron Mobility Transistor Membranes. Byoung Sam Kang¹, Suku Kim¹, Fan Ren¹, J.W. Johnson², R. J. Therrien², P. Rajagopal², J. C. Roberts², E. L. Piner², K. J. Linthicum², S. N. G. Chu³, K. H. Baik⁴, Brent Gila⁴, Cammy Abernathy⁴ and Stephen Pearton⁴; ¹Chemical Engineering, University of Florida, Gainesville, Florida; ²Nitronex, Raleigh, North Carolina; ³Multiplex Inc., South Plainfield, New Jersey; ⁴Material Science, University of Florida, Gainesville, Florida.

AlGaN/GaN high electron mobility transistors (HEMTs) show a strong dependence of source/drain current on the piezoelectric polarization induced two dimensional electron gas (2DEG). The spontaneous and piezoelectric polarization induced surface and interface charges can be used to develop very sensitive but robust sensors for the detection of pressure changes. The changes in the conductance of the channel of an AlGaN/GaN HEMT membrane structure fabricated on a Si substrate were measured during the application of both tensile and compressive strain through changes in the ambient pressure. The conductivity of the channel shows a linear change 6.4×10^{-2} mS/bar for application of compressive(tensile) strain from vacuum(10mTorr) to pressure (40-200psi) conditions. The AlGaN/GaN HEMT membrane-based sensors appear to be promising for pressure sensing applications.

9:15 AM **A8.3**

Realization of Multicompositional Mg_xZn_{1-x}O Based Metal-Semiconductor-Metal UV Detector on Quartz and Sapphire. Shiva Hullavarad¹, R. D. Vispute^{1,2}, S. Dhar¹, T. Venkatesan¹ and I. Takeuchi¹; ¹Center for Superconductivity Research, University of Maryland, College Park, Maryland; ²Bluewave Semiconductors, Baltimore, Maryland.

MgZnO is a novel oxide based UV sensitive material. The band gap of Mg_xZn_{1-x}O can be tuned by varying the composition of Mg to achieve band gaps corresponding to UV-A, UV-B, UV-C regions of UV spectrum. This material is of significant importance for various applications in flame sensors, UV index monitors and missile plume detection. The interesting property that makes this material unique is its existence in multiple phases for different Mg compositions. This allows picking up desired Mg composition corresponding to suitable UV sensitive window and growing on lattice matched substrate. In this paper we present the growth of MgZnO on non-conventional substrates like quartz and on sapphire for comparison of the device reliability. MgZnO films are characterized by X-Ray Diffraction, UV-Visible spectroscopy and Rutherford Back Scattering - channeling techniques. We are reporting for the first time the highly oriented growth of MgZnO on quartz by Pulsed Laser Deposition technique with a RBS channeling yield of 50% showing highly ordering. The morphology of the films is studied by Atomic Force Microscopy. The metal-semiconductor-metal device was fabricated on the MgZnO film to study the device response under proper UV irradiation

9:30 AM **A8.4**

Temperature Dependence of Electrical Conduction Properties in Boron Carbide Thin Films. Manuel J. Diaz, C. C. Ilie and S. Adenwalla; Physics and Astronomy and Center for Materials Research and Analysis, University of Nebraska, Lincoln, Nebraska.

The semiconducting form of Boron Carbide has been well established [1]. Uses for this material include the formation of true solid-state thermal neutron detectors [2]. Here we investigate the potential of BC for a high temperature semiconductor [3] by measuring the temperature dependence of the electrical conductivity. Thin films of p-type boron-carbon, approximately 300 nm thick, were deposited on Al₂O₃ (012) substrates using plasma-enhanced chemical vapor deposition (PECVD). The precursor compound used was Orthocarbonane (*closo*-1,2-dicarbadoecaborane; C₂B₁₀H₁₂) without further boron doping. X-ray diffraction indicates that the boron carbide deposited is polycrystalline and contains numerous polytypes. Resistance measurements of the boron carbide films were performed over a wide range of temperatures, 30 K to 450 K. The resistivity at room temperature was found to be of the order of 10⁵ ohm cm, and the temperature dependence shows an exponential decrease with temperature. The exponential behavior of the conductivity changes slope for temperatures higher than 140 K. We interpret these regions above and below the transition point as corresponding to those for the extrinsic and freeze out regions. Activation energies were calculated to be 0.04 eV and 0.12 eV below and above the transition point respectively. We will present temperature dependent Hall measurements and Raman spectroscopy to further elucidate the

structure and conductivity of these samples. This work is partially funded by the State of Nebraska, the U.S. Department of Energy National Nuclear Security Administration Office of Nonproliferation Research and Engineering [NA-22] through Pacific Northwest National Laboratory and the U.S Office of Naval Research N00014-04-1-0605.
[1]Dowben, PA, et. al.; J. Appl. Phys. 72(10): 4925 (1992)
[2]Robertson, BW, et. al.; App. Phys. Lett. 80(19): 3644 (2002)
[3]Adenwalla, S, et. al.; App. Phys. Lett. 79(26): 4357 (2001)

10:15 AM ***A8.5**

Perovskite Oxide Based Novel Sensors and Integration.

J. Narayan and Ashutosh Tiwari; Materials Science & Engineering, North Carolina State University, Raleigh, North Carolina.

During the last few years there has been a great demand for sensitive infrared detectors for a variety of applications in thermal imaging, night vision, biomedical imaging etc. Present technology has focused on mercury cadmium telluride as detector material. Though quite efficient, this material is difficult to process and control its composition due to Hg segregation. Other material, which is used quite commonly, is Indium Gallium Arsenide. But, one major drawback in both of these materials systems is that they require cooling. Because of this each IR detector has to have its own thermoelectric cooler, which increases the cost of these detectors tremendously and also poses a serious hurdle in the miniaturization of these detectors for on-chip applications in next generation microelectronics and optoelectronics applications. Therefore it is highly desirable to find new infrared sensitive materials with better response (with smaller signal to noise ratio) without any cooling requirement, which can be integrated with microelectronic devices. Recently we have developed some very interesting materials and structures, which show excellent IR sensory response even at room temperature, without any cooling requirement [1,2]. These structures are based on transition metal oxides, particularly NdNiO₃ and LSMO. Both of these oxides have perovskite structure and exhibit very rich electrical characteristics. NdNiO₃ undergoes a charge-transfer Metal-Insulator (M-I) transition as a function of temperature. Value of M-I transition temperature (TM-I) can be tuned upto room temperature by changing the epitaxial strain in the film or by partially replacing Ni by Fe in NdNiO₃. Because of the occurrence of M-I transition just close to RT, these materials provide excellent opportunity for applications in room temperature infrared detection. In this talk we will discuss some of our very important recent results on NdNiO₃ and LSMO based materials and structures. Excellent infrared detection characteristics of these structures will be discussed. An unique technique, based on our patented Domain Matching Epitaxy[3], will be described for integrating these structures with silicon substrates for on-chip IR detection. 1. Ashutosh Tiwari and J. Narayan Applied physics letters 83, 1773, 2003. 2. Ashutosh Tiwari and J. Narayan Applied physics letters 80, 4039, 2002. 3. J. Narayan, U.S. Patent No. 5, 406, 123 (April 11, 1995); J. Narayan, Journal of Applied Physics, 93, 278, 2003.

10:45 AM **A8.6**

Photonic Crystal Enhanced MEMS Infrared Gas Sensors.

Martin U. Pralle, Mark P. McNeal, Irina Puscasu, Anton C. Greenwald, James T. Daly and Edward A. Johnson; Ion Optics, Inc., Waltham, Massachusetts.

By modifying the structure of bulk silicon, from polished wafer to unique 2D photonic crystal of air holes in a metal coated silicon medium, we have transformed an infrared transparent material into a structure that vigorously absorbs infrared radiation at a discrete narrow band. Similarly, when heated this material generates tuned narrowband IR radiation with wavelength commensurate with the periodicity of the lattice. We have integrated this photonic crystal enhanced (PCE) technology into a MEMS thermal hot filament device to generate wavelength specific narrow band infrared emitters, detectors and sensor systems built directly on a silicon chip. By tuning the radiation to the absorption energy of a gas of interest we have implemented single component nondispersive infrared (NDIR) sensors for carbon dioxide and other IR absorbing gases. We envision that this technology will enable and enhance many other opto-electronic devices including thermal energy conversion, imaging and lighting.

11:00 AM **A8.7**

Pulse shape study of chemical vapor deposited diamond alpha particle detectors. Sigen Wang¹, Paul Sellin¹ and Annika

Lohstroh¹; ¹Department of Physics, University of Surrey, Guildford, United Kingdom; ²Department of Physics, University of Surrey, Guildford, United Kingdom; ³Department of Physics, University of Surrey, Guildford, United Kingdom.

Chemical vapor deposited (CVD) diamond is increasing used for the fabrication of high energy radiation detectors due to its high radiation hardness, low leakage current, low dielectric constant, high electron and hole mobilities. However, the presence of inherent defects and the

polycrystalline nature of CVD diamond strongly affects its detection performance, and to date there is still little to be known on the role of the defects on the detection behaviors. In order to clarify this subject, in this paper, pulse shapes recorded under positive and negative biases using a 241Am alpha particle source are detailed analyzed and compared. The pulse time evolution of the CVD diamond detectors are found to speed up with increasing the bias voltage under alpha particle irradiation, this might be responsible for the effects of the defects incorporated in diamond. The detection mechanism is discussed in terms of the experimental results.