

# SYMPOSIUM NN

## Chemical Processing of Dielectrics, Insulators, and Electronic Ceramics

November 29 – December 1, 1999

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\* Invited paper

**8:45 AM \*NN1.1**

DESIGN, SYNTHESIS AND CHARACTERIZATION OF PRECURSORS. William S. Rees, Jr., Georgia Institute of Technology, Atlanta, GA.

Ferroelectric and other high dielectric constant metal oxides are sought-after currently for a variety of applications in the electronics industry. To meet the demand of preparation of these interesting materials in a manner compatible with traditional silicon-based fabrication procedures, chemical vapor deposition routes are sought for film growth. Compounds having high vapor phase stability are necessary as precursors for these applications. Additionally, in general, it is preferred to utilize compounds in a liquid state, due to the more rapid re-establishment of equilibrium at a liquid-vapor interface, compared to that found at a solid-vapor interface. This combination of desired molecular properties, in turn, presents a great challenge to the coordination chemist. Several of the metals of interest for these uses reside in groups 2 - 5. Common design features are emerging for the ligands best suited for attachment to these metals for subsequent utilization in the deposition of metal oxides. In order to achieve coordinative saturation of the relatively high ionic radii exhibited by most of these elements, multidentate, monoanionic ligands are relied upon. In the past, most often, homoleptic ligand sets have been employed, thereby reducing the chance for ligand scrambling to occur during the growth process. Such disproportionation processes have been credited, in previous work, with the observation of a temporal decay in vapor pressure of heteroleptic compounds. In some interesting new developments, it has been found that heteroleptic compounds possess sufficient vapor phase integrity to permit their evaluation as CVD precursors. These, and related, results will be presented in this lecture.

**9:15 AM NN1.2**

NEW LIQUID PRECURSORS FOR CHEMICAL VAPOR DEPOSITION (CVD) OF ALUMINUM AND GALLIUM NITRIDES. Seán T. Barry, Roy G. Gordon and Valerie A. Wagner, Harvard University Chemical Laboratories, Cambridge, MA.

New precursors were developed for CVD of aluminum nitride (AlN) and gallium nitride (GaN) at low temperatures. Synthetic methods for the new materials will be reported, along with their analyses and spectral characterization. The precursors are volatile (180 mTorr at 45-55 C), low-viscosity (5-7 centipoise) liquids, so they are more convenient as vapor sources than the previously available solid sources. They are thermally stable up to temperatures well above their vaporization temperatures, so their vaporization is highly reproducible and leaves no residue. They are not pyrophoric, so they are safer to handle than the previously available pyrophoric liquid precursors. AlN films formed by reaction with ammonia at around 200 C are amorphous, transparent insulators that are good barriers to diffusion of water, oxygen and other materials. CVD results for GaN will also be reported.

**10:00 AM NN1.3**

LOW TEMPERATURE CHEMICAL VAPOR DEPOSITION OF TITANIUM NITRIDE THIN FILMS WITH HYDRAZINE AND TETRAKIS-(DIMETHYLAMIDO)TITANIUM. Carmela C. Amato-Wierda, Edward T. Norton Jr., The University of New Hampshire, Materials Science Program, Durham, NH; Derk A. Wierda, Saint Anselm College, Department of Chemistry, Manchester, NH.

Hydrazine has been used as a precursor along with tetrakis-(dimethylamido)titanium for the low temperature chemical vapor deposition of TiN thin films between 50°C and 200°C at growth rates between 5 to 35 nm/min. The Ti:N ratio in these films is approximately 1:1. They contain 2% carbon, and varying amounts of oxygen up to 36% as a result of diffusion after air exposure. Moreover, low temperature growth is improved with hydrazine-ammonia mixtures containing as little as 1.9% hydrazine. The Ti:N ratio in these films is almost 1:1 and they contain little carbon or oxygen according to RBS and XPS. The TiN films grown from pure hydrazine or the hydrazine-ammonia mixture have some crystallinity according to x-ray diffraction and their resistivity is on the order of  $10^4 \mu\omega\text{cm}$ . The low temperature growth is attributed to the weak N-N bond in hydrazine and its strong reducing ability. Studies of film growth processing parameters (temperature, pressure, reactant ratio, residence time) will be presented.

**10:15 AM NN1.4**

SILANE ACTIVATION BY TETRAKIS-(DIMETHYLAMIDO) TITANIUM (TDMAT) AND AMMONIA DURING CHEMICAL

VAPOR DEPOSITION OF TITANIUM-SILICON-NITRIDE THIN FILMS. Carmela C. Amato-Wierda, Edward T. Norton, Jr., University of New Hampshire, Materials Science Program, Durham, NH; Derk A. Wierda, Saint Anselm College, Dept. of Chemistry, Durham, NH.

Ti-Si-N is a refractory amorphous ternary nitride that is a promising candidate for diffusion barrier applications in future metallization schemes of integrated circuits. One chemical vapor deposition method for the production of Ti-Si-N uses tetrakis-dimethylamidotitanium (TDMAT), silane, and ammonia at 450°C. It is interesting that silane reacts at these low temperatures given that silane and ammonia typically require temperatures between 600-700°C to form silicon nitride. Molecular beam mass spectrometry has been used to observe the activation of silane, predominantly in the gas phase, during the chemical vapor deposition of Ti-Si-N thin films using TDMAT, silane, and ammonia at 450°C. The extent of silane reactivity was dependent upon the relative amounts of TDMAT and ammonia. Ti-Si-N thin films were deposited using similar process conditions as the molecular beam experiments. RBS and XPS were used to determine the atomic composition of these films. The variations of the Ti:Si ratio as a function of TDMAT and ammonia flows were consistent with the changes in silane reactivity under similar conditions.

**10:30 AM NN1.5**

PHOTO-CHEMICAL GROWTH OF THIN FILMS FROM SOLID STATE PRECURSORS. Wai Lo, K. Salama, Texas Center for Superconductivity and Department of Mechanical Engineering, University of Houston, Houston, TX.

Various solid state Metallo-organic materials (MO) are known to undergo dissociations through different mechanisms, such as direct bond breaking, reaction with atmosphere and transfer of excited electrons to neighboring acceptors, when irradiation by UV-Vis photons. This leads to the possibility of developing low temperature and non-vacuum based film deposition techniques from pre-coated MO precursors if the growth process of films from decomposed precursors under UV-Vis irradiation is well-studied. With the potential of integrating film deposition and photolithography steps, such techniques would be most suitable for applications in electronics industries. This presentation concentrates on establishing the dissociation conditions of selected MO and the photo-activation conditions of film growth from dissociated precursors in some metal and oxide systems. Results of structural characterization by X-ray diffractometry, microstructural analysis by scanning electron microscopy and electric transport properties will be discussed. These results will be correlated with the film deposition conditions.

**10:45 AM NN1.6**

$\beta$ -SUBSTITUTED ETHYL SILSESQUIOXANES: NEW PRECURSORS FOR SiO<sub>2</sub> AND MODIFIED SiO<sub>2</sub> FILMS. Karin A. Ezbiansky, Donald H. Berry, Lisa K. Figge, Hai-Lung Dai, Department of Chemistry, University of Pennsylvania, Philadelphia, PA; Russell J. Composto, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA; Barry Arkles, Gelest, Inc., Tullytown, PA.

Silsesquioxanes containing  $\beta$ -substituted ethyl groups,  $\text{RSiO}_{1.5}$  ( $\text{R} = \text{CH}_2\text{CH}_2\text{X}$ ;  $\text{X} = -\text{Cl}, -\text{Br}, -\text{O}_2\text{CCH}_3$ ), are processible polymers that undergo conversion to silica or organically modified silicas (ORMOSILs) under mild thermal or photochemical conditions. In contrast to typical alkyl or aryl silsesquioxanes, the  $\text{CH}_2\text{CH}_2\text{X}$  moiety undergoes facile extrusion of ethylene with formation of Si-X groups. Subsequent rapid hydrolysis leads to complete condensation of the SiO<sub>2</sub> network. Smooth, crack-free dielectric films 500-5000 Å thick have been prepared on silicon wafers, and have been analyzed by a variety of techniques including RBS, SEM, AFM, SIMS, and ESCA. These films exhibit high thermal and oxidative stability. Recent efforts have focused on the chloride-free  $\beta$ -acetoxylethylsilsesquioxane system. Additionally, results from the examination of base-catalyzed thermal conversion routes will be presented.

**11:00 AM NN1.7**

EFFECT OF PRECURSOR DOPES ON PHASE FORMATION OF LEAD STRONTIUM ZIRCONATE-TITANATE SOLID SOLUTIONS. Tatyana Teplytskaya, Olga Demirskaya, Victor Cherginets, Valeriy Ishchuk and Tatyana Rebrova, Institute for Single Crystals, Kharkov, UKRAINE.

The traditional solid phase processing of oxide ceramic materials from oxide mixtures proceeds through the formation of different intermediate compounds (phases), therefore, it requires the sequence of grinding and annealing (synthesis) stages. It is obviously, that achieving maximal yield of final phase after the first sintering stage allows to reduce expenses for the processing. The purpose of present work is to study the effect of precursor dopes on phase formation at the synthesis of  $(\text{Pb}_{0.75}\text{Sr}_{0.25})(\text{Zr}_{0.65}\text{Ti}_{0.35})_3$

(PSZT). The dopes

1. final single phased PSZT sintered at 1200°C, 10 mass.%;
2. wet co-precipitated hydroxides, 2 mass.%;
3. hydroxides from item 2 treated by acetic acid, 2 mass.%;
4. hydroxides from item 2 treated by alcohol solution of abietic acid, 2 mass.%;

were entered in starting oxide mixture. Annealed samples were studied by X-ray phase analysis, DTA and dilatometry. The use of all mentioned dopes led to formation of single-phased product at sintering temperatures efficiently lower than for undoped samples, but the best results were obtained for acetate and abietate dopes. In these cases the formation of single phase product was observed at 1000°C.

Annealing of latter dopes (usual precursors for film application) is known to lead to direct formation of final single phased product at efficiently lowered temperatures. Results obtained may be explained by formation of fine dispersed PSZT phase particles (nuclei) in the bulk. Latter favor the direct complete transformation of initial oxides in PSZT.

It has been shown at first that the decrease of phase formation temperature at the solid phase synthesis may be achieved without the use of dopes containing foreign elements.

#### 11:15 AM NN1.8

GROWTH OF MgO BY METAL-ORGANIC MOLECULAR BEAM EPITAXY. Feng Niu, Brent.H.Hoerman and Bruce.W.Wessels, Department of Materials Science and Engineering, Northwestern University, Evanston, IL.

In recent years there has been increasing interest in the deposition of ultra-thin film oxide insulators. In the present work, MgO thin films were deposited on (100) Si substrates by metal-organic molecular beam epitaxy (MOMBE). Magnesium beta-diketonates were used as the precursors and an oxygen RF plasma was used as the oxidant. The typical growth temperature was 700°C. Films from 20 to 500 nm were grown at a deposition rate of 0.2 to 0.8 nm/min. Composition analysis by EDAX and microstructure characterization by transmission electron microscopy indicated that the films are both stoichiometric and phase-pure MgO. The films were polycrystalline. Scanning Auger microprobe analysis indicated no carbon incorporation in the films. Atomic force microscopy indicated that the films had a smooth surface morphology. The index of refraction was 1.71.

#### 11:30 AM NN1.9

STUDY ON ZrO<sub>2</sub> DEPOSITED DIRECTLY ON Si AS AN ALTERNATIVE GATE DIELECTRIC MATERIAL. Wen-Jie Qi, Renee Nieh, Byoung Hun Lee, Laegu Kang, Yongjoo Jeon and Jack C. Lee, Microelectronics Research Center, The University of Texas at Austin, Austin, TX.

As MOSFET channel lengths are scaled down to 0.1µm and beyond, ultra-thin (<15Å) gate oxide is required. Conventional thermal oxide reaches its physical limit because of the excessive direct tunneling current. It is believed that for a gate oxide thickness thinner than 15Å, high-k dielectric is needed. Research has been conducted on various high-k materials such as Barium Strontium Titanate, TiO<sub>2</sub>, and Ta<sub>2</sub>O<sub>5</sub>, etc. However, none of these materials are thermodynamically stable in contact with Si. A barrier layer is required. There has been an attempt to use a single layer structure for its process simplicity and compatibility with the integrated circuit processes. ZrO<sub>2</sub> has been predicted thermo-dynamically stable in contact with Si; it has a dielectric constant of 25 and bandgap of 7.8eV. It can be etched by HF solution. In this paper, we will present both electrical and reliability characteristics as well as material properties involving ZrO<sub>2</sub> dielectric material. XPS, SIMS, TEM, AFM have been used to characterize the film. C-V, I-V, SILC, and TDDB characteristics have been measured. Equivalent oxide thickness of 12.6Å with a leakage of  $\approx 10^{-3}$  A/cm<sup>2</sup> at 1V has been obtained. This film exhibits excellent reliability properties such as low charge trapping rate and good time-dependent dielectric breakdown.

#### SESSION NN2: DIELECTRICS

Chair: Sanjeev Kaushal

Monday Afternoon, November 29, 1999  
Room 312 (H)

#### 1:30 PM NN2.1

DIELECTRIC AND LEAKAGE CURRENT PROPERTIES OF (Ta<sub>2</sub>O<sub>5</sub>)<sub>0.922</sub>-(TiO<sub>2</sub>)<sub>0.078</sub> THIN FILMS PREPARED BY LIQUID SOURCE DELIVERY METALORGANIC CHEMICAL VAPOR DEPOSITION. C.S. Chang, T.B. Wu, Dept of Material Science and Engineering, National Tsing Hua University, TAIWAN, R.O.C.; W. C. Shih, L.L. Chao, Vanguard International Semiconductor Corporation, TAIWAN, R.O.C.

(Ta<sub>2</sub>O<sub>5</sub>)<sub>0.922</sub> - (TiO<sub>2</sub>)<sub>0.078</sub> thin films (~20nm) were prepared on nitridized poly-Si electrode by liquid source delivery metalorganic chemical vapor deposition in this study. Precursors of Ta(C<sub>2</sub>H<sub>5</sub>O)(C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub> and Ti(C<sub>3</sub>H<sub>7</sub>O)<sub>2</sub>(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>2</sub> were separately delivered to a flash vaporizer through a double-syringe liquid pump (MKS DLI-25B). The temperature of the vaporizer was maintained at 200J, and all gas lines were heated at 180J to prevent the source from condensation. The reactor pressure and substrate temperature were maintained at 1 torr and 400J, respectively. The results reveal that the dielectric constant of the films critically depends on the post annealing condition. The highest value of effective dielectric constant is about 47 for such a film combined with a 2nm SiN film on the bottom. Compared to pure CVD Ta<sub>2</sub>O<sub>5</sub> thin films, this significant enhancement in dielectric constant is obtained by adding a small quantity of TiO<sub>2</sub>. The leakage current of the (Ta<sub>2</sub>O<sub>5</sub>)<sub>0.922</sub>-(TiO<sub>2</sub>)<sub>0.078</sub> thin film was significantly reduced to 10<sup>-8</sup> A/cm<sup>2</sup> at 1.7MV/cm after rapid thermal annealing in oxygen (RTO) at 850J for 120secs, which was also better than that of the pure Ta<sub>2</sub>O<sub>5</sub> film, i.e. 10<sup>-7</sup> A/cm<sup>2</sup> at 1.7MV/cm, under the same heat treatment condition. Excellent leakage current characteristic with high capacitance values suggest that the (Ta<sub>2</sub>O<sub>5</sub>)<sub>0.922</sub> - (TiO<sub>2</sub>)<sub>0.078</sub> thin film is a more promising material than the pure Ta<sub>2</sub>O<sub>5</sub> film in fabricating the capacitor for Gbit DRAM.

#### 1:45 PM NN2.2

HIGH DENSITY PLASMA ETCHING OF Ta<sub>2</sub>O<sub>5</sub> -SELECTIVITY TO Si AND EFFECT UV LIGHT ENHANCEMENT. K.P. Lee, H. Cho, R.K. Singh, S.J. Pearton, Univ. of Florida, Dept. of Materials Science and Engineering, Gainesville, FL; C. Hobbs and P. Tobin, Motorola, Austin, TX.

Etch rates up to 2000 Å•min<sup>-1</sup> or Ta<sub>2</sub>O<sub>5</sub> were achieved in both SF<sub>6</sub>/Ar and Cl<sub>2</sub>/Ar discharges under Inductively Coupled Plasma conditions. The etch rates with N<sub>2</sub>/Ar or CH<sub>4</sub>/H<sub>2</sub>/Ar chemistries were an order of magnitude lower. There was no effect of post deposition annealing on the Ta<sub>2</sub>O<sub>5</sub> etch rates, at least up to 800 °C. Selectivities to Si of ~1 were achieved at low source powers, but at higher powers the Si typically etched 4-7 times faster than Ta<sub>2</sub>O<sub>5</sub> UV illumination during ICP etching in both SF<sub>6</sub>/Ar and Cl<sub>2</sub>/Ar produced significant enhancements (up to a factor of 2) in etch rates due to photo-assisted desorption of the TaF<sub>x</sub> products. The UV illumination is an alternative to employing elevated sample temperatures during etching to increase the volatility of the etch products and may find application where the thermal budget should be minimized during processing.

#### 2:00 PM \*NN2.3

MOCVD OF HIGH-K DIELECTRICS AND CONDUCTIVE METAL NITRIDE THIN FILMS Yoshihide Senzaki, Schumacher, Carlsbad, CA; Richard F. Hamilton, Air Products and Chemicals, Allentown, PA; Kimberly G. Reid, Chris C. Hobbs and Rama I. Hegde, Motorola, Austin, TX.

A known liquid mixture of (Et<sub>2</sub>N)<sub>3</sub>Ta=Net and (Et<sub>2</sub>N)<sub>3</sub>Ta[EtN=C(H)Me] was studied to deposit Ta<sub>2</sub>O<sub>5</sub> and TaN thin films by chemical vapor deposition. Films were deposited at temperatures below 400°C using oxygen for oxide and ammonia for nitride, respectively. X-ray diffraction analysis revealed that as-deposited amorphous tantalum oxide films were converted to hexagonal Ta<sub>2</sub>O<sub>5</sub> after annealing under oxygen, while tantalum nitride thin films contained cubic TaN as deposited. The thermal stability, low viscosity, and sufficient volatility of the precursor allows its delivery by direct liquid injection, which results in both high deposition rates and high uniformity of deposited films. The CVD processes, surface analysis and electrical characterization of the deposited films will be discussed. Development of other metal oxide/nitride CVD precursors will also be discussed in this presentation.

#### 3:00 PM \*NN2.4

GROUP IV OXIDES AS HIGH PERMITTIVITY GATE INSULATORS. S.A. Campbell<sup>1</sup>, B. He<sup>1</sup>, R. Smith<sup>2</sup>, T. Ma<sup>1</sup>, N.

Hoilien<sup>1</sup>, C. Taylor<sup>2</sup>, and W. L. Gladfelter<sup>2</sup>, <sup>1</sup>Dept. of Electrical and Computer Engineering, <sup>2</sup>Dept. of Chemistry, Univ of Minnesota, Minneapolis, MN.

Increasing MOSFET performance requires scaling, the systematic reduction in device dimensions. Tunneling leakage, however, provides an absolute scaling limit for SiO<sub>2</sub> of about 1.5 nm. Power limitations and device reliability are likely to pose softer limits slightly above 2 nm. We have investigated the use of high permittivity materials such as TiO<sub>2</sub>, ZrO<sub>2</sub>, and their silicates as potential replacements for SiO<sub>2</sub>. We have synthesized nitrate titanium (Ti(NO<sub>3</sub>)<sub>4</sub>) and nitrate zirconium (Zr(NO<sub>3</sub>)<sub>4</sub>) as hydrogen and carbon free deposition precursors and have used them to deposit various films. Several problems arise in the use of high permittivity films including the formation of an interfacial low permittivity layer and current leakage in the high permittivity films. In this talk we will discuss the leakage

mechanisms of these layers and the impact of carbon free precursors on the leakage current. We will also discuss the use of amorphous and thermodynamically stable films, contrasting their behavior to more conventional unstable polycrystalline high permittivity layers. We have also carried out considerable surface nitridization work to retard the formation of the interfacial layer and will discuss the effects of both thermal and remote plasma surface nitridization treatments on the properties of the film stack. This work was supported by Motorola and Texas Instruments through a Semiconductor Research Corporation Research Customization Award (Contract #BJ479) and by IBM through a University Partnership Award.

### 3:30 PM NN2.5

**SILICON CLEANING METHODS COMPARED AT METAL CONCENTRATIONS BELOW  $1E10$  ATOMS/CM<sup>2</sup>.** Joseph Ilardi, Rajananda Saraswati, George Schwartzkopf, Mallinckrodt Baker, Inc., Research and Technology Development Department, Phillipsburg, NJ.

An alkaline aqueous silicon wafer cleaner has been developed which reduces trace metal contamination levels on p-type unpatterned silicon wafers to below  $1E10$  atoms/cm<sup>2</sup> without acidic cleaning. This patented technology uses a specially formulated buffering system consisting of an oxidation resistant chelating agent and salt of a weak acid. The aqueous cleaner maintains a stable pH of about 9.5 over a wide range of dilutions, temperatures, hydrogen peroxide concentrations and bath aging times. A single-step bath, megasonic bath or spray clean with this formulation leaves the chemical oxide on the silicon wafer surface free of particles, atomically smooth, free of organics and lower in trace metal contamination levels than similar surfaces cleaned with conventional formulations. An analytical method was developed which allows the reliable detection of trace metals on silicon wafer surfaces down to  $1E8$  atoms/cm<sup>2</sup> for aluminum, calcium, copper, iron, nickel, sodium and zinc. The procedure uses an ICP-MS with a concentric nebulizer and a desolvator. The acids used were ultrapure to keep the blanks to a very minimum and analyses were run in a class 10 clean room. The trace metals on the wafer were extracted using known amounts of ultrapure acids and were directly aspirated using a special arrangement with the concentric nebulizer. The J. T. Baker cleaner was compared to and outperformed the conventional RCA-1&2 clean and dilute RCA-1&2 chemistries using ultrapure ammonium hydroxide, hydrochloric acid and hydrogen peroxide.

### 3:45 PM NN2.6

**PREPARATION OF HIGH QUALITY ULTRA-THIN GATE DIELECTRICS BY CAT-CVD AND CATALYTIC POST-DEPOSITED ANNEAL.** Hidekazu Sato<sup>1,2</sup>, Akira Izumi<sup>1</sup> and Hideki Matsumura<sup>1</sup>; <sup>1</sup>JAIST, Ishikawa, JAPAN, <sup>2</sup>FUJITSU Limited, Mie, JAPAN.

The lowering growth temperature of gate dielectrics films with high permittivity such as silicon nitride ( $Si_3N_4$ ) films is a key for the fabrication of the future ultra large scale integrated circuits (ULSI) with deep sub-micron dimensions. In the catalytic chemical vapor deposition (Cat-CVD) method, the deposition gases such as a gaseous mixture of silane ( $SiH_4$ ) and ammonia ( $NH_3$ ) are decomposed by catalytic cracking reactions with a heated tungsten catalyst placed near substrates, and  $Si_3N_4$  films are formed at substrate temperatures (T<sub>sh</sub>) around 300°C without using plasma. In the present work, the feasibility of Cat-CVD system for deposition and also improvement of ultra thin gate dielectrics is studied. Particularly, the effect of post deposited anneal (PDA) by using hydrogen ( $H_2$ )-decomposed species or  $NH_3$ -decomposed species formed by catalytic cracking of  $H_2$  or  $NH_3$  are investigated. The C-V characteristics are measured by MIS diode for the 4.5nm-thick Cat-CVD  $Si_3N_4$  and 8nm-thick sputtered  $SiO_2$  for comparison. It is found that a small hysteresis loop is seen in the C-V curve of  $Si_3N_4$  and  $SiO_2$  films as deposited. However, it is improved by the PDA at 300°C using  $H_2$  or  $NH_3$ , and the hysteresis loop completely disappears from the C-V curve for both films. This result demonstrates that the PDA is a powerful technique to improve quality of insulating films, such as Cat-CVD  $Si_3N_4$  and even sputtered  $SiO_2$  films. In addition, by PDA the leakage current of  $Si_3N_4$  films with 2.8nm equivalent oxide thickness is decreased by three orders of magnitude,  $1 \times 10^{-8}$  A/cm<sup>2</sup> for 0.5MV/cm, and the breakdown field is increased from 4.8MV/cm to 11.2MV/cm. It is concluded that the PDA technology in Cat-CVD system is the promising candidates for fabrication of gate dielectrics in ULSI.

### 4:00 PM NN2.7

**LOW TEMPERATURE AND LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF SILICON NITRIDE THIN FILMS FOR MICROELECTRONIC APPLICATIONS.** Wen Yu, Spyridon Skordas, Di Wu, Haral Efstathiadis and Alain E. Kaloyeros, New York State Center for Advanced Thin Film Technology and Department of Physics, The University at Albany - SUNY, Albany, NY.

Silicon Nitride growth technology has been incorporated in microchip fabrication (very large and ultra large scale integration VLSI / ULSI),

thin film transistors (TFT), solar energy conversion (solar cells) and many other microelectronic applications of a rapidly increasing market. Nevertheless, the silicon nitride production technologies currently in use impose considerable limitations. Low pressure chemical vapor deposition (LPCVD) occurs at relatively high temperature (>700°C) and plasma enhanced chemical vapor deposition (PECVD), although occurring at temperatures below 350°C, is partially damaging the devices due to ion bombardment. In the present work, successful low temperature and low pressure chemical vapor deposition of silicon nitride thin films is reported on 8 inches silicon wafers. The use of a novel silicon precursor, silicon tetraiodide ( $SiI_4$ ) has led to the deposition of high quality silicon nitride thin films at temperatures as low as ~350°C. Analysis and characterization of the produced films with respect to the dependence of the film properties on deposition parameters has been performed by means of Auger Electron Spectroscopy (AES), Rutherford Backscattering Spectroscopy (RBS), Fourier Transform Infrared (FTIR), Nuclear Reaction Analysis (NRA), Ellipsometry, capacitance-voltage (C-V), and current-voltage (I-V) measurements.

### 4:15 PM NN2.8

**THE COMPOSITION AND STRUCTURE OF ULTRATHIN CHEMICAL OXIDES: A PHOTOEMISSION AND INFRARED STUDY.** Joseph Eng Jr., Robert L. Opila, Yves J. Chabal, Joseph M. Rosamilia, Martin L. Green, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

Because gate oxides are usually grown following wet chemical processing, gate oxide quality depends upon the nature of the initial wet oxides and their evolution during furnace growth or rapid thermal oxidation. We have studied as-grown and mildly oxidized chemical oxides using Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS). Several chemical treatments have been used to oxidize  $Si(100)$  samples following an initial HF strip: (1) SPM, a sulfuric acid/peroxide mixture (2) 4:1:1 water : hydrogen peroxide : ammonium hydroxide (SC1), 4:1:1 water : hydrogen peroxide: hydrogen chloride (SC2), called standard RCA; (3) a modified RCA that includes a HF strip between SC1 and SC2; (4) ozonated water; and (5) concentrated nitric acid. All chemical oxides are characterized by a fairly large number of defects, sub-stoichiometric oxide, and voids. For example, modified RCA oxides are the thinnest, most defective, and hydrocarbon contaminated of the films. Annealing the modified RCA films in vacuum shows that the hydrocarbon contaminants containing oxygen decompose and further oxidize the Si. Furthermore, annealing in low pressures of oxygen removes voids, as determined by an increased separation of the frequencies of the transverse optical and longitudinal optical modes. In contrast, the least defective and least contaminated films are found following the sulfuric acid and ozonated water cleans. Annealing these oxides in oxygen shows only a small increase in the separation of the LO and TO modes, indicating that there are relatively fewer voids initially. We will discuss how the chemical quality of these oxide films affects transistor gate electrical performance.

### 4:30 PM NN2.9

**A NEW METHOD FOR THE PREPARATION OF TIN DIOXIDE: POTENTIAL FOR MODIFIED PROPERTIES.** Georges Denes, Arnaud Gueune, Eva Laou, Stephane Le Huerou, Abdualhafed Muntasar and Frederic Nicolas, Concordia University, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mossbauer Spectroscopy, and Laboratories for Inorganic Materials, Montreal, Quebec, CANADA.

The sol-gel method is usually used for the preparation of nanophase  $SnO_2$ . This involves the precipitation of a stannic gel by hydrolysis of a tin(IV) compound containing labile tin-ligand bonds. We have designed a new method that consists in oxidizing tin(II) to tin(IV) and simultaneously hydrolyzing the tin-ligand bonds. The new method consists in oxidizing tin(II) to tin(IV) by addition of hydrogen peroxide to an aqueous solution of  $SnF_2$ . This results in a substitution of fluorine by oxygen, and a precipitate of hydrated tin(IV) oxide  $SnO_2 \cdot nH_2O$  ( $n = ca. 2$ ) is obtained. This phase is nanophase and can be subsequently dehydrated without recrystallization under mild heating. Recrystallization takes place slowly at higher temperatures, due to the ceramic properties of  $SnO_2$ , which make it thermally very stable, and the slow recrystallization makes it possible to tailor the desired average particle size. In addition, control of its properties might be possible by modifying its chemical properties. It can be made to contain tin(II) or tin(IV) fluorides/oxide fluorides by modifying the preparation conditions, mainly the  $H_2O_2/SnF_2$  ratio.

### NN3.1

DEPOSITION OF SiO<sub>2</sub>:F:C FILMS WITH LOW DIELECTRIC CONSTANT AND WITH HIGH RESISTANCE TO ANNEALING. Jorge Lubguban Jr., Yoshihiro Kurata, Takao Inokuma, Seiichi Hasegawa, Dept of Electronics, Faculty of Technology, Kanazawa Univ, Kanazawa, JAPAN.

Continuing trends in ULSI lead to shrinking device dimensions to less than 0.25  $\mu\text{m}$ . As device size decreases, problems due to wiring capacitance like propagation delay, crosstalk noise and power dissipation occur. One way to effectively solve these problems is to find a suitable material with low dielectric constant ( $k$ ). SiO<sub>2</sub>:F films with a dielectric constant of 3.3 has been widely investigated. Recently, PTFE,  $\alpha$ -C:F, porous materials and organic silica with low  $k$  are studied. However, problems with thermal stability, water absorption and step coverage arise for these films. In these study, carbon doping to SiO<sub>2</sub>:F films were investigated. The films were deposited using a plasma enhanced chemical vapor deposition (PECVD) device. The gases used consisted of SiH<sub>4</sub>, O<sub>2</sub>, and CF<sub>4</sub> with fixed flow rates. Carbon was added by mixing CH<sub>4</sub> to the gas mixture. The films were deposited with a temperature of 300°, rf power of 20 watts and pressure of 0.17 Torr. The deposition times were adjusted in order to obtain films with almost the same thickness of 350 nm. The obtained films were also annealed with increasing temperature up to 800°C to test its thermal stability. XPS, FT-IR, ESR, stress, C-V and I-V characteristics were measured. Results show that incorporation of carbon decreases the dielectric constant of SiO<sub>2</sub>:F from 3.35 to 2.9. Furthermore, the water resistivity was improved as shown by the decreasing absorption intensity of Si-OH band with increasing CH<sub>4</sub> flow rate. The new films were more resistant to annealing as can be observed from the stability of Si-CH<sub>3</sub> band and  $k$  up to a temperature of 600°C. In addition, effects of water absorption decreases with annealing temperature.

### NN3.2

ULTRA LOW K DIELECTRICS VIA OXIDATION OF OCTAHYDRIDO SILSESQUIOXANE. T.L. Krebsbach Jr., R.M. Laine, University of Michigan, Dept. of Materials Chemistry, Ann Arbor, MI.

From studies involving the oxidation of sublimed octahydrido silsesquioxane, thin films were developed that possess the potential to be used for the next generation of microelectronic insulating materials. The oxidation of octahydrido silsesquioxane results in the formation of a well-defined, high surface area (> 250 m<sup>2</sup>/g), nano-porous silica structure maintaining the cubic silsesquioxane as the base unit. The material exhibits a low K value (> 3) due to the ordered porosity (4 and 10 nm). The structure and properties of the material have been characterized using DSC, TGA, FTIR, TEM, BET and PALS.

### NN3.3

SYNTHESIS OF HIGH-K TITANIUM OXIDE THIN FILMS FORMED BY METALORGANIC DECOMPOSITION. Hisashi Fukuda, Yoshihiro Ishikawa, Seigo Namioka and Shigeru Nomura, Department of Electrical and Electronic Engineering, Muroran Institute of Technology, Hokkaido, JAPAN.

Owing to the scale down of ULSIs, the thickness of SiO<sub>2</sub> films must be decreased to increase transconductance and charge storage capacity of the MOSFETs. However, a serious problem of the device scaling arises in the oxide thinning due to enhanced tunneling current and defect density, resulting in lower breakdown strength and poor yields. A possible solution is to replace the SiO<sub>2</sub> with large dielectric constant materials to enable the use of comparatively thicker films. Among the new dielectric films, titanium oxide (TiO<sub>2</sub>) is one of promising dielectrics as a possible SiO<sub>2</sub> replacement. We have successfully formed the high-k ( $\epsilon_{\text{max}}=76$ ) TiO<sub>2</sub> films by metalorganic decomposition (MOD), having precise composition control, large area deposition, simple and nonvacuum process. In this paper, we demonstrate on the TiO<sub>2</sub> structure, dielectric properties and MOSFET characteristics will be demonstrated. First, 5 wt% MOD solution of Ti-containing alkoxide (Ti(i-OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) was directly deposited onto the Si by the spin coating technique. After deposition, the films were dried in air, then pre-annealed at 400°C for 30 min. Crystallization was carried out in an oxygen at temperatures ranging from 600 to 1000°C for 30 min. The crystallinity of the films was evaluated using a Raman spectroscopy and X-ray diffraction (XRD) measurements. The TiO<sub>2</sub>/Si interface structure was analyzed using a spectroscopic ellipsometry. The C-V and I-V measurements were conducted on films in a MOS structure with Al gate electrodes. n-channel MOSFETs were also fabricated with a channel length and

gate width of 30  $\mu\text{m}$  and 2.25 mm, respectively.

Raman spectra of TiO<sub>2</sub> films indicate that the pre-annealed and crystallized TiO<sub>2</sub> films have the anatase and rutile structures depending on the crystallization temperature. The XRD patterns for TiO<sub>2</sub> films showed the anatase structures with peaks of (101), (112), (200) and (211). These results indicate that the TiO<sub>2</sub> films prepared from MOD have the crystalline structure with anatase as its main component and have a low crystallization temperature of 600°C. The results of spectroscopic ellipsometry indicate the interfacial SiO<sub>2</sub> growth, resulting in obtaining stacked TiO<sub>2</sub>-SiO<sub>2</sub> structure. The C-V curves show that the capacitance is a maximum at 700°C annealing, however, decreases with increasing annealing temperature. This behavior originates directly from the increase in the thickness of the interfacial SiO<sub>2</sub> layer. The dielectric constant annealed at 600°C remains at 24, whereas, the dielectric constant increases sharply and a maximum ( $\epsilon_{\text{max}}=76$ ) in the samples annealed at 700°C, which is exactly the crystallization temperature detected from the Raman spectra. The dielectric constant decreases rapidly when annealing temperature increases above 800°C. This is due to stoichiometric change with increasing temperature. The I<sub>D</sub> V<sub>D</sub> characteristics of MOSFET with Pt-gate/TiO<sub>2</sub>(66.9nm)/SiO<sub>2</sub>(12.3 nm)/Si structure have been investigated. The gate bias starts from 0 to 5 V by 1 V step. The saturation current is linearly dependent on gate voltage. The subthreshold characteristics indicate the inverse slope of about 80 mV/decade, which corresponds to the theoretical values. This work was supported by the Foundation of Material Science and Technology of Japan (MST Foundation).

### NN3.4

ANALYSIS OF A TEOS/OXYGEN PLASMA: INFLUENCE OF ENERGY AND PARTICLE FLUX ON THE DEPOSITION PARAMETERS. Maria L. Pereira da Silva and Ana N. Rodrigues da Silva, Laboratorio de Sistemas Integraveis Departamento de Engenharia Eletronica USP, SP, BRAZIL; Jorge J. Santiago-Aviles, University of Pennsylvania, Dept. of Electrical Engineering, Philadelphia, PA.

In this work we looked at deposition parameters such as rate and film microstructure during the plasma enhanced CVD processing of TEOS Si (OCH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub> + O<sub>2</sub>. This is a multi-component oxide due to the inevitable accidental inclusion of carbonaceous contaminants. We decided to characterize the plasma parameters, namely the electron energy (from 50 to 600 eV), and the flux of the reactive species. The deposition chamber was modified by the introduction of a stainless steel tubular ring between the electrodes, such that when a positive bias is applied it is possible to inject electrons into the plasma. A dual role for the tubular ring is the transport of oxygen to different locations in the plasma, to monitor the influence of the oxygen flux on deposition. The experimental results showed that by increasing the voltage bias on the ring from 0 to 600 V, the oxide deposition rate is enhanced. For low precursor concentration (TEOS), the deposited films shows micro-structural improvement as evidenced by FTIR spectroscopy. We monitored the formation of carbon compounds by their RAMAN signature, and one can see that for small ring bias, the concentration of carbon contaminants is large and it decreases with increasing electron energy. A reaction model consistent with our experimental results must consider the need of oxygen ions in the oxidation of the precursor. Since an increase in the electron flux hinders the formation of oxygen ions, a pressure decrease must be utilized to improve the chemical properties of the film such as the formation of carbonaceous contaminants. The inescapable conclusion is that higher density plasmas favor the processing of organo-silicates.

### NN3.5

MOCVD OF COBALT, MANGANESE AND ZIRCONIUM OXIDES THIN FILMS. Stefano Bozza, Giovanni Carta, Gilberto Rossetto, Pierino Zanella, Inst of Inorganic Chemistry and Technology and Advanced Materials, CNR, Padua, ITALY; Davide Barreca, Gianni Cavinato, Dept of Inorganic Chemistry and Analytical Chemistry, Padua, ITALY.

MOCVD of Co, Mn and Co-Zr oxide thin films has been carried out by using respectively Co(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, Mn(hfac)<sub>2</sub>(THF)<sub>2</sub> (hfac= hexafluoroacetylacetonate) and (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub> mixed to Co(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> as precursors. Oxygen and oxygen-water vapor mixture atmospheres have been employed as reactant gas. The oxides were deposited onto stainless steel, aluminum, silicon (100) and glass substrates in the temperature range 450° - 550°C. Co(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> under oxygen atmosphere at 450°C deposited Co<sub>3</sub>O<sub>4</sub>, but with a low deposition rate and poor morphology. Under oxygen and water vapor atmosphere the quality of the layers was improved and the deposition rate increased. XPS of the material deposited on glass showed the binding energy peaks characteristic of both Co<sup>2+</sup>, Co<sup>3+</sup> and O<sup>2-</sup>, with no implication of the presence of C species. X-ray powder diffraction highlighted a preferred crystallite orientation that depends strongly on the substrate. Mn<sub>3</sub>O<sub>4</sub> deposition depended also from the reactant gas; the layer obtained in oxygen-water vapor atmosphere

being superior to those obtained in pure oxygen atmosphere. XPS indicated the presence of  $Mn^{2+}$ ,  $Mn^{3+}$  and  $O^{2-}$  in the deposited material, with no detection of fluorine and carbon contamination.  $Mn_3O_4$  in  $\gamma$ -crystalline phase was determined by x-ray diffraction. By decomposing together both  $Co(C_5H_5)_2$  and  $(C_5H_5)_2Zr(CH_3)_2$  in oxygen-water vapor atmosphere, the structure of the deposit corresponds to a mixture of the two oxide compounds.

### NN3.6

GROUP III METAL OXIDE AND SULFIDE MATERIALS. Paul O'Brien, David J. Otway, Jin-Ho Park, Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UNITED KINGDOM.

Indium oxide, gallium oxide, indium sulfide and gallium sulfide have been prepared from single-source precursors by various chemical vapor deposition techniques. Single-source precursors have shown the most promise for depositing such materials by thin film growth techniques, such as metalorganic chemical vapour deposition (MOCVD). The thin films obtained were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis by X-ray (EDAX) and X-ray Photoelectron Spectroscopy (XPS).

### NN3.7

MOLECULAR BEAM MASS SPECTROMETRY STUDIES OF THE THERMAL DECOMPOSITION OF TETRAKIS (DIMETHYL-AMINO)TITANIUM. Carmela C. Amato-Wierda, Edward T. Norton Jr., University of New Hampshire, Materials Science Program, Durham, NH; Derk A. Wierda, Saint Anselm College, Dept of Chemistry, Manchester, NH.

Tetrakis(dimethylamino)titanium (TDMAT) is an important precursor for TiN, TiCN, and TiSiN thin films in chemical vapor deposition. In order to better understand how the gas phase chemistry influences the formation of these films, the decomposition of TDMAT has been studied in a high-temperature flow reactor (HTFR) by molecular beam mass spectrometry (MBMS). Two kinetic regimes have been observed as a function of temperature. Rate expressions and mechanistic implications will be presented. Further studies are in progress to identify the gas phase species relevant to the decomposition mechanism of TDMAT.

### NN3.8

LCVD OF  $CN_x$  LAYERS. B. Ivanov, Univ of Chemical Technology and Metallurgy, Sofia, BULGARIA; M. P. Tarassov and S. Vassilev, Central Laboratory of Electrochemical Power Sources.

Thin  $CN_x$  films were obtained by Laser Chemical Vapor Deposition (LCVD) using the focused beam (200 $\mu$ m) of copper bromide vapor laser with wavelengths of 510 and 578 nm on monocrystalline Si (100) in vacuum system. The laser average power was in the range 4-10 W with repetition rate - 20 kHz and the pulse duration - 60 ns.  $C_3N_3(CF_3)_3$  -2,4,6 Tris(trifluoromethyl)1,3,5-triazine was used as a precursor at pressure range - 1 - 15 Torr. The basic process parameters were varied in the ranges: scanning speed from 50 $\mu$ m/s to 400  $\mu$ m/s and substrate temperature of 100 and 400 $^\circ$ C, respectively. Nanosecond dynamics of chemical reaction in the focus spot create unsteady state condition and enhanced formation of metastable phases. The main advantageous of this precursors is that it is hydrogen free, volatile and non explosive. The possible decomposition products are  $CF_3$  and  $CN_x$  species which could favored formation of crystalline structure by etching of amorphous phase by  $CF_3$  radicals. The morphology of the deposited films investigated by Scanning Electron Microscopy (SEM) shows well defined fine grain structure. The analysis of the layers by Energy Dispersive X-ray analysis (EDX) and Auger Electron Spectroscopy (AES) shows  $CN_x$  composition with different value of x. Carbon to nitrogen ratio reach 1:1 at some process parameters. The crystallinity of the layers was approved by X-Ray Diffraction (XRD). The several diffraction peaks resulting from the crystalline planes of the synthesized  $CN_x$  phases possess the d-spacing values of 3.0531  $\text{\AA}$ , 2.5014  $\text{\AA}$ , 1.9217  $\text{\AA}$ , 1.8824  $\text{\AA}$ , 1.6104  $\text{\AA}$ , 2.1057  $\text{\AA}$  and 2.2981  $\text{\AA}$ . The chemical bond structure was investigated by Fourier Transform Infra Red analysis (FTIR) in absorption and reflection modes. Strong absorption at 1071  $cm^{-1}$  and 1161  $cm^{-1}$  can be assigned to N-(C)3 bonds. Absorption at 808  $cm^{-1}$  we attached to the formation of C-Si bonds.

## SESSION NN4: FERROELECTRICS

Chair: Sanjeev Kaushal  
Tuesday Morning, November 30, 1999  
Room 312 (H)

### 8:30 AM \*NN4.1

IMPORTANCE OF SOFT SOLUTION-PROCESSING FOR ADVANCED INORGANIC MATERIALS TO SUSTAINABLE

DEVELOPMENTS. Masahiro Yoshimura, Tokyo Institute of Technology, Materials and Structures Laboratory, Center for Materials Design, Yokohama, JAPAN.

Modern human society has been developed by huge amounts of production, use and waste of advanced artificial materials, and by huge consumption of energies and resources. The flow of those materials and energies seems to be already saturated or even over saturated on the earth. World consumption of energy has reached to critical sizes: 10% of total photosynthesis energy and 0.1 - 0.5% of total atmospheric (wind, wave, tide, etc.) energy. Therefore, we must eliminate rather than increase those materials and energies flows. Recycling of materials (wastes) is possible when we put more energies to the recycling process than the production/fabrication process, but it brings about more thermal contamination. In order to prevent such thermal contamination, we must consider total processing for useful materials from mining and up-grading of raw materials, then production/fabrication, usage, transportation, waste and until cycling/recycling of products by environmentally friendly ways. Based upon the fact that almost all materials and energies in nature have been cycled essentially by water cycle on the earth, we can conclude that fabrication and processing of artificial (industrial) materials must be based upon water (solution) flow to minimize the loads to the environment. According to above consideration, we are proposing Soft Solution Processing (SSP) which means direct (preferably than indirect) fabrication of inorganic materials with desired composition, structure, properties, shape, size, location from aqueous solution at a mild temperature and pressure condition. The SSP is more environmentally friendly but more difficult than "dry" processing using gas(es), vapor(s), molecule(s), cluster(s), atom(s), ion(s), in vacuum gas and/or in plasma. This is because that species in a solution has been stabilized by solvation (hydration in water) energy, therefore they have smaller driving force ( $\Delta G$ ) for the reaction but require higher activation energy ( $\Delta G^*$ ) than highly energetic species in dry processings. However, SSP becomes possible when we could choose certain systems and conditions. For example, we have succeeded to fabricate thin/thick films of  $BaTiO_3$ ,  $SrTiO_3$ ,  $(Ba, Sr, Ca)WO_4$ ,  $LiCoO_2$ ,  $LiNiO_2$  on various substrates in alkaline solutions at 100-200 $^\circ$ C, sometimes even at RT, with/without electrochemical (anodic) oxidation. They are well-crystallized and deposited on the substrates, thus no post-heating has been required in contrast to so-called "sol-gel" coated and electrophoretically deposited films. Double layer film of  $BaTiO_3/SrTiO_3$  has also been fabricated at 150 $^\circ$ C using a flow-cell apparatus. Details of preparation and properties of them will be presented.

### 9:00 AM \*NN4.2

APPLICATION OF PULSED INJECTION MOCVD TO THE DEPOSITION OF DIELECTRIC AND FERROELECTRIC OXIDE LAYERS AND SUPERLATTICES. Jean-Pierre Senateur, Johannes Lindner, Francois Weiss, Catherine Dubourdieu, Carmen Gimenez, LMGP, ENS de Physique de Grenoble INPG, Saint Martin D'Heres, FRANCE; Kui Yu Zhang, Université de Marne La Vallé, FRANCE; Adolfas Abrutis, Vilnius University, LITHUANIA.

The technique used for the control of the injection of fuel in thermal motors has been applied to the generation of active gases for MOCVD layers deposition. The principle is a sequential injection of micro amounts (few milligrams) of a solution of organic precursors into an evaporator, where a flash volatilization occurs. The system is quite different from the other liquid sources commonly used for MOCVD process, the main differences are : - The vapor flow rate is controlled by a computer which accurately determines the frequency of injection and the size of the droplets. - The system uses a flash evaporation : only one source containing a solution of the precursors is required for the synthesis of complex compounds. - The injector is a low cost element, which can be easily changed. Multilayers or superlattices of complex compounds are readily obtained with several injectors connected to the same evaporator. A wide variety of compounds and multilayers have already been grown using this new CVD source (from simple Al, Ce, Mg Ta, Ti, Y or Zr oxides to more complex compounds like  $YBa_2Cu_3O_7$ ,  $PrBa_2Cu_3O_7$  or  $(La,Sr)MnO_3$ ). With two injection sources working sequentially, stackings like  $YBa_2Cu_3O_7/CeO_2$  or  $YBa_2Cu_3O_7/SrTiO_3$  double layers have been in-situ obtained. Amorphous  $Ta_2O_5/SiO_2$  multilayers or  $SrTiO_3/BaTiO_3$  and  $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$  superlattices have been easily synthesized with this process. We will focus in this presentation on the results obtained on the deposition of dielectric and ferroelectric layers and multilayers.

### 10:00 AM NN4.3

SELECTION AND DESIGN OF PRECURSORS FOR THE MOCVD OF LEAD SCANDIUM TANTALATE. Anthony C. Jones, Timothy J. Leedham, Hywel O. Davies, Inorgtech Limited, Mildenhall, Suffolk, UNITED KINGDOM; Michael J. Crosbie, Peter J. Wright, Dennis J. Williams, Defence, Evaluation and Research Agency, Great Malvern, Worcs, UNITED KINGDOM; Paul O'Brien, Kirsty A. Fleeting,

The ferroelectric material lead scandium tantalate,  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$  has a high figure of merit for operation in uncooled thermal imagers. As a consequence of this, it has potential for use in a number of infrared device applications such as night sight technologies, fire detection and medical diagnosis. Thin films have been grown by a number of deposition technologies including sputtering, sol-gel deposition and metalorganic chemical vapour deposition (MOCVD). However, progress in the MOCVD of  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$  has been restricted by a lack of suitable precursors with the appropriate physical properties and decomposition characteristics. For instance, in liquid injection MOCVD, the high temperatures required to evaporate successfully the conventional Sc source  $\text{Sc}(\text{thd})_3$  (thd = 2,2,6,6-tetramethyl-3,5 heptanedionate) can lead to decomposition of co-precursors such as  $\text{Pb}(\text{thd})_2$  and  $\text{Ta}(\text{OEt})_5$ . This can result in oxide films with poor compositional uniformity, and to blockages in the evaporator and reactor inlet system. In this paper, it is shown how the modification of the molecular structure of the  $\text{Ta}(\text{OR})_5$  and Sc  $\beta$ -diketonate precursors leads to precursors which have more compatible physical properties, and which can also deposit the individual oxide thin films ( $\text{PbO}$ ,  $\text{Sc}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ ) in a similar temperature regime. The use of these Ta and Sc precursors with more compatible properties offers the potential for a significant advance in the MOCVD of  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ . Results on the deposition of thin films of the individual oxides and of  $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$  will be presented.

#### 10:15 AM NN4.4

SOL-GEL SYNTHESIS OF  $\text{BaTiO}_3$  BASED FILMS FOR PHOTONIC AND MICROWAVE APPLICATIONS. V. Fuflyigin, H. Jiang, F. Wang, P. Vakhutinsky, W. Ho, J. Zhao, P. Norris, NZ Applied Technologies, Woburn, MA; J. Chi, M/A-COM, Lowell, MA.

The processing of barium titanate based materials recently attracted a lot of attention due to of the unique combination of the ferroelectric, electro-optic, and photorefractive properties. The growth of thin and thick films of  $\text{BaTiO}_3$  is of special interest because of their potential applications in a number of photonic and electronic devices. However, there are issues to be addressed: reduction of the growth temperature, growth of several  $\mu\text{m}$  thick films, improvement of the optical, electro-optic and dielectric properties. This paper reviews the current status of our research on the growth of  $\text{BaTiO}_3$  films with an emphasis on resolving the aforementioned problems. The effect of the processing conditions and precursor chemistry on the films properties will be discussed. We will also tackle the use of low-melting fluxes as a possible approach to promote the crystallization process. As a result of the process optimization, the growth temperature of  $\text{BaTiO}_3$  films was brought down to  $550^\circ\text{C}$ . High-quality films of  $\text{BaTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  have been prepared on  $\text{LaAlO}_3$ , R- and C-sapphire substrates. Second order electro-optic coefficient measured in  $\text{BaTiO}_3$  film on R-sapphire was as high as  $0.65 \Sigma 10^{-16} (\text{m/V})^2$ . This value was found to be strongly dependent on substrate material, films orientation and composition. The dielectric properties, such as  $\epsilon$  and Q-factor were measured in the 10 kHz-1GHz range. Variations related to the processing conditions and composition were observed. The applications of the prepared films for etalon-based EO devices and microwave devices are also discussed.

#### 10:30 AM NN4.5

FERROELECTRIC COMPOSITE OF  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x=0.2, 0.4, 0.6$ ) WITH  $\text{Al}_2\text{O}_3$  AND  $\text{MgO}$  SYNTHESIZED BY SOL-GEL METHOD. Pramod K. Sharma, K.A. Jose, V.V. Varadan and V.K. Varadan, Research Center for the Engineering of Electronics and Acoustic Materials, Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA.

The low dielectric, low loss tangent and high tunability are the prime characteristics of the ceramic materials e.g. Barium strontium titanate (BST), to use in phased array antenna systems, therefore, an alternative fabrication of composite is disclosed in this work. Sol-gel processing was adopted to prepare  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  for three values of  $x$  i.e. 0.2, 0.4 and 0.6. The obtained powders were calcined and sintered at 1100 and 1250 C respectively. Further the composite of Barium strontium titanate (BST) with the  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  were fabricated (named BST-M). The weight ratio of BST may range from 90%wt to 40%wt, to metal oxide e.g.  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ , from 10%wt-60%wt. Ball milling was used for the mixing of powders using zirconia balls. The dielectric properties, were determined by using impedance analyzer in the frequency range from 1kHz to 1MHz. This work presents a complete study on the effect of metal oxides on the dielectric constant, tangent loss and tunability of the final BST-M composites.

#### 10:45 AM NN4.6

DEPOSITION OF CRACK-FREE  $\text{BaTiO}_3$  AND  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  FILMS OVER 1  $\mu\text{m}$  THICK VIA SINGLE STEP DIP-COATING.

Single step sol-gel deposition of thick coating films suffers crack formation, and the critical thickness, the maximum film thickness achievable without crack formation, is often less than 0.1  $\mu\text{m}$ . When the final film thickness desired is much larger than the critical thickness, which is often the case, cycles of gel film deposition and heat-treatment should be carried out, which is not a realistic way in industrial production. In the present study, incorporation of polyvinylpyrrolidone (PVP) in gel films is demonstrated to be effective in enhancing the critical thickness of  $\text{BaTiO}_3$  and  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  films.  $\text{BaTiO}_3$  and  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  films were prepared from alkoxide and acetate solutions containing PVP by depositing gel films on silica glass substrates via dip-coating and heating them at several hundred  $^\circ\text{C}$ . In all cases the deposition was made in a single step, and crack-free films over 1  $\mu\text{m}$  thick could be obtained. The critical thickness was affected by the content and molecular weight of PVP, where higher molecular weight PVP was found to be more effective in enhancing the critical thickness. The resultant films were relatively dense in SEM scale and transmitting visible light. Denser and more transparent films resulted when the gel films were heated stepwisely at low to high temperatures.

#### 11:00 AM NN4.7

DIELECTRIC PROPERTIES AND STOICHIOMETRIC CONTROL OF HYDROTHERMAL  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ , AND  $\text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3$  THIN FILMS. Mark A. McCormick, Ryan K. Roeder and Elliott B. Slamovich, Purdue University, School of Materials Engineering, West Lafayette, IN.

Polycrystalline  $\text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3$  (BST) thin-films were processed hydrothermally on Ag-coated glass substrates at temperatures below  $100^\circ\text{C}$  by reacting films of a titanium metallo-organic precursor (titanium dimethoxy dineodecanoate, TDD) in alkaline solutions containing  $\text{Ba}^{2+}$  and/or  $\text{Sr}^{2+}$ . Two reaction sequences were used: either the TDD was reacted directly in solution, or the TDD was pyrolyzed in air at temperatures up to  $500^\circ\text{C}$  prior to reaction in solution. The pre-pyrolysis route converted the precursor into nanocrystalline and/or amorphous  $\text{TiO}_2$ . Film stoichiometry deviated from solution composition, with a preferred incorporation of  $\text{Sr}^{2+}$  into the perovskite lattice. The reaction kinetics were slower for the pre-pyrolyzed films, and as the rate of conversion to BST decreased, preferred  $\text{Sr}^{2+}$  incorporation became more favorable. Dielectric properties were examined over the temperature range  $20^\circ\text{C}$  to  $140^\circ\text{C}$  to determine the role of phase stoichiometry. Results are correlated to those obtained from bulk properties of powders processed in a similar manner.

#### 11:15 AM NN4.8

HYDROTHERMAL PREPARATION OF  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  THIN FILMS FROM Ti-Zr METALLIC ALLOYS ON SILICON SUBSTRATES. Chang-Tai Xia, V.M. Fuenzalida and R.A. Zarate, Universidad de Chile, Facultad de Ciencias Físicas y Matemáticas, Departamento de Física, Santiago, CHILE.

Hydrothermal preparation of  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  thin films from sputtered Ti-Zr metallic alloys deposited on silicon wafer substrates was achieved. A Ti-Zr 66:34 at.% alloy target was used as the sputtering source. X-ray diffraction indicated that a 4 hour hydrothermal treatment in 0.5 M  $\text{Ba}(\text{OH})_2$  aqueous solution at  $150^\circ\text{C}$  was sufficient to fully react a  $\sim 55 \text{ nm}$  Ti-Zr alloy thin film deposited on the silicon substrate. A 2 hour treatment in 1 M solution resulted in a similar degree of crystallinity in the thin films. However, the morphology, roughness, and cracks in the formed  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  films were different for the different preparation conditions. Surface analysis suggested the diffusion of Ti and/or Zr during the hydrothermal treatment. Preliminary capacitance measurements revealed a dielectric constant of  $\sim 200$  for the hydrothermal 300 nm  $\text{Ba}(\text{Ti,Zr})\text{O}_3$  films. The formation mechanism of the films will be discussed.

#### 11:30 AM NN4.9

SUPPRESSION OF FERROELECTRIC PHASE TRANSITION IN HYDROTHERMAL  $\text{BaTiO}_3$  FINE PARTICLES BY LATTICE DEFECTS. Tu Lee, Ilhan A. Aksay, Princeton University, Department of Chemical Engineering and Princeton Materials Institute, Princeton, NJ; Boris E. Vugmeister, Princeton University, Department of Chemistry, Princeton, NJ; Nan Yao, Princeton University, Princeton Materials Institute, Princeton, NJ.

The size effect is a widely accepted concept that there is a critical size above which  $\text{BaTiO}_3$  particles are tetragonal and ferroelectric, and below which particles are cubic and paraelectric. This is of growing importance for the fundamental understanding of the ferroelectric properties of  $\text{BaTiO}_3$  in microelectronic devices. However, the inconsistency of the critical size in the literature ranging from 15 to 200 nm suggests that the ferroelectric properties of  $\text{BaTiO}_3$  particles

are not a function of the Euclidean geometry alone. This further evidenced by our capability of synthesizing 250 and 500 nm sized cubic BaTiO<sub>3</sub> particles hydrothermally at 80°C and the production of 90 nm sized tetragonal BaTiO<sub>3</sub> powders hydrothermally at 240°C by others. We found that 700°C treated 250 nm hydrothermal BaTiO<sub>3</sub> powders with the size unchanged had a higher effective dielectric constant and less lattice strains than the virgin powders. Therefore, we propose that it is not just the size (higher structural level) but the means to reduce the size that alters the lattice (lower structural level) which, in turn, affects the ferroelectric properties. The thermal cycle from 25° to 700°C and 1400°C showed that the stabilization of cubic phase is associated mainly with hydroxyl-induced cation vacancies. Their concentrations are related to the degree of completion of hydrolysis and condensation in the hydrothermal process. The random field theory is also used to describe the suppression of the ferroelectric phase transition and the increase in lattice strain induced by lattice defects.

#### 11:45 AM NN4.10

##### MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF HYDROTHERMALLY DERIVED BaTiO<sub>3</sub> THIN FILMS.

Mark A. McCormick, Elliott B. Slamovich, Purdue University, School of Materials Engineering, West Lafayette, IN.

Polycrystalline BaTiO<sub>3</sub> thin-films were processed hydrothermally on Ag-coated glass substrates at temperatures below 100°C by reacting films of a titanium metallo-organic precursor (titanium dimethoxy dineodecanoate, TDD) in alkaline solutions containing Ba<sup>2+</sup>. Two reaction sequences were used: either the TDD was reacted directly in an aqueous solution of Ba(OH)<sub>2</sub>, or the TDD was pyrolyzed in air at temperatures up to 500°C prior to reaction in Ba(OH)<sub>2</sub>. The pre-pyrolysis route converted the precursor into nanocrystalline and/or amorphous TiO<sub>2</sub>. Capacitors were assembled using photolithography to apply top electrodes, and dielectric properties were examined in the context of film microstructure and thickness. Direct reaction of the precursor produced films composed of several layers of particles, with dielectric constants of approximately 10. When the precursor was pre-pyrolyzed before reacting, the resulting BaTiO<sub>3</sub> films were composed of a single layer of impinging particles, and dielectric constant values were as high as 250. Thin-film porosimetry indicated that reaction conditions have a strong effect on film density, and that elimination of porosity was the key to obtaining high dielectric constant films.

#### SESSION NN5: BATTERIES/FUEL CELLS

Chair: Anthony C. Jones

Tuesday Afternoon, November 30, 1999

Room 312 (H)

#### 1:30 PM NN5.1

GROWTH OF RuO<sub>x</sub> THIN FILMS BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION. Younsoo Kim, Kyung-Cheol Jeong, Jae-Hyun Joo, Jong-Bum Park, Jae-Sung Roh, Jin-Won Park, Process Team, Central Research Laboratory, LG Semicon, Cheongju, KOREA.

RuO<sub>x</sub> (x=0 or 2) thin films were deposited on several substrates by metal organic chemical vapor deposition (MOCVD) at deposition temperatures of 250-400°C. Tris(6-methyl-2,4-heptadionato)-ruthenium(III), [Ru(mhd)<sub>3</sub>, Ru(C<sub>8</sub>H<sub>13</sub>O<sub>2</sub>)<sub>3</sub>], was used as a MO source because of its high vapor pressure, good thermal stability, and liquid property at room temperature. Ru(mhd)<sub>3</sub> dissolved in methanol was evaporated in a heated vaporizer. Argon gas was used as a carrier gas to deliver the evaporated source to the process chamber and O<sub>2</sub> gas was employed as an oxidant gas. The smooth and well-adherent RuO<sub>x</sub> films had very low resistivities. No films could be deposited without oxidant gas whereas RuO<sub>x</sub> films were deposited with a small amount of oxygen. The microstructure was greatly dependent on deposition conditions of the RuO<sub>x</sub> films. By the XRD analysis, polycrystalline RuO<sub>x</sub> films were deposited. The addition of O<sub>2</sub> gas significantly affected the growth and phase of the films. No film could be grown without O<sub>2</sub> addition whereas RuO<sub>x</sub> films could be deposited with O<sub>2</sub> addition. We could deposit the Ru or RuO<sub>2</sub> films by controlling amount of O<sub>2</sub> gas. Without O<sub>2</sub> addition small particles were found on the substrates. The surface of Ru films was the smoother than that of RuO<sub>2</sub> films. RuO<sub>x</sub> films were consisted of well-developed columnar grains. The composition of RuO<sub>x</sub> films was analyzed using XPS to determine carbon contents. The XPS results showed that the carbon couldn't be found in RuO<sub>x</sub> films. The resistivity of RuO<sub>2</sub> films was slightly larger than that of Ru films. RuO<sub>x</sub> films had very low resistivities.

#### 1:45 PM NN5.2

IRON SULFIDE THIN FILMS PREPARED FROM SINGLE-SOURCE PRECURSORS BY LP-MOCVD. Paul O'Brien, David J.

Otway and Jin-Ho Park Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UNITED KINGDOM.

Iron sulfide films have been prepared from single-source precursors by various chemical vapour deposition techniques. Single-source precursors have shown the most promise for depositing such materials by thin film growth techniques, such as metal-organic chemical vapour deposition (MOCVD). The thin films obtained were characterised by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Analysis by X-ray (EDAX) and X-ray Photoelectron Spectroscopy (XPS).

#### 2:00 PM NN5.3

VOLATILE LIQUID PRECURSORS FOR THE CHEMICAL VAPOR DEPOSITION (CVD) OF THIN FILMS CONTAINING ALKALI METALS. Randy N.R. Broomhall-Dillard, Roy G. Gordon and Jeffrey T. Barton, Harvard University Chemical Laboratories, Cambridge, MA.

The first volatile, liquid compounds of alkali metals were synthesized and used for the CVD of materials containing alkali metals. Amides of the type MN(R<sup>1</sup>)(SiMe<sub>2</sub>R<sup>2</sup>) and MN(SiMe<sub>2</sub>R<sup>2</sup>)<sub>2</sub> [M = Li, Na, K; R<sup>1</sup> = t-butyl, t-amyl; R<sup>2</sup> = ethyl, n-propyl, i-propyl, n-butyl, i-butyl, n-hexyl, n-octyl] were made and characterized. The lithium and sodium amides were prepared via the deprotonation of the parent amine using butyl lithium and sodium hydride, respectively. The potassium amides were formed by transamination of potassium bis(trimethylsilyl)amide with the parent amines. For example, lithium bis(n-propyldimethylsilyl)amide was prepared from butyl lithium and bis(n-propyldimethylsilyl)amine and was distilled as a clear, colorless liquid at 130 C (150 mTorr) having a viscosity of 23 cP at 40 C. These alkali metal amides can be used as convenient liquid sources for CVD of mixed metal oxides containing alkali metals, such as the non-linear optical material lithium niobate, lithium-containing materials for battery electrodes, electrochromic tungsten bronzes, and the pyroelectric and ferroelectric material potassium tantalate.

#### 2:15 PM NN5.4

GROWTH AND STUDIES OF Li(Mn, Co) OXIDES FOR BATTERY ELECTRODES. Santender Nieto-Ramos and Maharaj S. Tomar, Physics Department, University of Puerto Rico, Mayaguez, PR; Ram S. Katiyar, University of Puerto Rico, San Juan, PR.

There is an interest in lithium intercalation oxide materials for cathodes in rechargeable batteries. We have synthesized (LiMOx) where M = Co, Mn with different Mn and Co ratios, by a less expensive solution route. Reagent grade hydroxides or acetates are used for lithium, manganese and cobalt, respectively, with methoxy ethenol and acetic acid as solvents. The powder with different compositions are achieved at annealing temperatures below 700°C. X-ray diffraction and Raman spectroscopic studies with temperature dependent dielectric properties of these materials will also be presented. Some thin film samples were also prepared by spin coating.

#### 2:30 PM NN5.5

FABRICATION OF CRACK-FREE La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-y</sub> MEMBRANES ON ASYMMETRIC POROUS CERAMIC SUPPORTS—EFFECTS OF A METALLIC COVERING. Cao Zhenan, Hong Liang, National Univ of Singapore, Dept of Chemical Engineering, SINGAPORE.

The La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3-y</sub> (LSCO) type materials with mixed electronic-oxygen ionic conductivity is a hot R&D subject for solid oxide fuel cells and for gas industry as the oxygen separation membrane. The main problem in the fabrication of LSCO membrane on the asymmetric porous ceramic support is the shrinkage mismatch between a green ceramic layer packed by fine powders and the porous support during sintering, which results in mismatch-induced cracking. A crack-free mesoporous LSCO thin membrane has been successfully fabricated onto asymmetric and macroporous ceramic substrates such as MgO and CeO in our laboratory by using the dip-coating method. The mesoporous LSCO thin membrane is an essential cushion layer for further fabricating a dense LSCO thin film, which is the goal of the processing. In order to avoid the muddy cracks, a metal-topping layer on the green LSCO powder coating is found most effective. The metal is required to have its melting point slightly lower than the sintering temperature of the LSCO material and is inactive to LSCO material during sintering. One of such metallic materials is silver. The silver top layer can be selectively and easily removed by immersing it into a specially formulated chemical solution. Controlling the composition of the colloidal suspension of LSCO powder used for forming the green deposit on the porous supports can also help to get the crack-free film. The morphology and microstructure of the crack-free LSCO thin film and the effect of using various LSCO colloids are studied by scanning electron microscopy, X-ray diffraction and gas permeation test.

**2:45 PM NN5.6**

CHEMICAL SYNTHESIS OF DOPED LaGaO<sub>3</sub> POWDERS BY THE CITRATE / PEG METHOD. A. Cuneŷt Tas, Heike Schluckwerder, Peter Majewski and Fritz Aldinger, Pulvermetallurgisches Laboratorium, Max-Planck-Institute für Metallforschung, Stuttgart, GERMANY.

Conditions of synthesis of the Sr- and Mg-doped LaGaO<sub>3</sub> powders of solid oxide fuel cell applications were studied by using the amorphous citrate/acetate and modified Pechini methods. Lanthanum nitrate, gallium nitrate, magnesium nitrate, strontium acetate, citric acid, acetic acid and ethylene glycol were used as the starting, reagent-grade chemicals in the powder synthesis experiments. The influence of cation concentrations in the solutions and the volume ratio of citric (or acetic) acid-to-ethylene glycol on powder phase purity, particle size and morphology were investigated. The characterization and chemical analysis of the synthesized LaGaO<sub>3</sub> precursors and calcined (700° to 1200°C) powders were performed by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), Fourier-transformed infra-red spectroscopy (FT-IR), and inductively-coupled plasma atomic emission spectroscopy (ICP-AES).

**SESSION NN6: SOLAR CELLS**

Chair: Anthony C. Jones  
Tuesday Afternoon, November 30, 1999  
Room 312 (H)

**3:30 PM \*NN6.1**

WET-CHEMICAL SYNTHESIS OF THIN-FILM SOLAR CELLS. Wet-Chemical Raffaella, William Junek, Rochester Institute of Technology, Dept of Physics, Rochester, NY; Joe Gorse, Tracy Thompson, Baldwin-Wallace College, Dept of Chemistry, Berea, OH; Al Hepp, Dave Hehemann, NASA Glenn Research Center at Lewis Field, Photovoltaics and Space Environments Branch, Cleveland, OH.

We have been working on the development of wet-chemical processing methods that can be used to create thin film photovoltaic solar cells. Electrochemical deposition methods have been used to produce copper indium gallium diselenide (CIGS) thin films on molybdenum and indium tin oxide (ITO) coated glass substrates. CIGS has an extremely high optical absorption coefficient, excellent radiation resistance, and good electrical conductivity; and thus has proved to be an ideal absorber material for thin film solar cells. Theoretically, the stoichiometric control provided by the electrodeposition process could be used to produce both n and p-type CIGS films with bandgaps ranging from approximately 1.1 eV to 1.5 eV. A series of compositionally different p-type CIGS films were produced by using different electrochemical deposition potentials. Cadmium sulfide (CdS) window layers were deposited directly on these CIGS films using a chemical bath process. CdS is a naturally n-type wide-bandgap semiconductor which has good transparency and is well lattice-matched to CIGS. The CdS films were grown as a function of bath temperature and pH, and deposition time. The structural and elemental properties of the individual CdS and CIGS films were characterized by x-ray diffraction and energy dispersive spectroscopy. The electrical behavior of the CdS on CIGS junctions was determined using current versus voltage and capacitance versus voltage measurements. We will discuss the performance of these devices based on the physical properties of their component films and the processing methods employed in their fabrication.

**4:00 PM NN6.2**

METALORGANIC CHEMICAL VAPOUR DEPOSITION OF CuM<sup>(III)</sup>E<sub>2</sub> (WHERE M<sup>(III)</sup> = Ga or In; E = S or Se) FROM COPPER, GALLIUM AND INDIUM DI-SULFIDE-/SELENO-CARBAMATES FOR SOLAR CELL DEVICES. Michael R. Lazell, John McAleese, Paul O'Brien and David J. Otway, Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UNITED KINGDOM.

Thin film(s) of the chalcopyrite materials CuM<sup>(III)</sup>E<sub>2</sub> (where M<sup>(III)</sup> = Ga or In; E = S or Se) have been grown by low-pressure metal-organic chemical vapour deposition (LP-MOCVD) and aerosol assisted chemical vapour deposition (AACVD) using the precursors M<sup>(III)</sup>(E<sub>2</sub>CNMe<sup>n</sup>Hexyl)<sub>3</sub> and Cu(E<sub>2</sub>CNMe<sup>n</sup>Hexyl)<sub>2</sub> (where M<sup>(III)</sup> = Ga or In; E = S or Se). Films were grown on glass, ITO, GaAs, InP, and Si between 300 - 450°C, and characterized by X-ray diffraction, optical spectroscopy (UV/Vis), EDAX, XPS, and (SEM) scanning electron microscopy. Recent work has included the deposition of these materials on Chemical Bath Deposited CdS for the construction of functional solar cells.

**4:15 PM NN6.3**

NEW APPROACHES TO CHEMICAL BATH DEPOSITION OF CHALCOGENIDES. John McAleese, Paul O'Brien, David J. Otway

and David S. Boyle, Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, London, UNITED KINGDOM.

We have been studying new approaches to the chemical bath deposition of chalcogenide containing materials where the solution is circulated over a heated substrate. In many ways this may be thought of as an analogous system to that in CVD except that the solution can be continuously circulated over the substrate. Thin films produced by this method may be used in solar cell devices or other optoelectronic applications. Thin films of, for example, CdS, ZnS and the ternary material Cd<sub>x</sub>Zn<sub>1-x</sub>S have been deposited, and the films have been characterized (and shown to be of high quality) by for instance XPS, SEM, XRD, RBS, UV/Vis spectroscopy. Other chalcogenide materials such as Bi<sub>2</sub>S<sub>3</sub>S are also being studied at this time.

**SESSION NN7: POSTER SESSION: FERROELECTRICS**

Chair: Anthony C. Jones  
Tuesday Evening, November 30, 1999  
8:00 P.M.  
Exhibition Hall D (H)

**NN7.1**

A STUDY ON HYSTERESIS EFFECT OF BARIUM STRONTIUM TITANATE THIN FILMS FOR ALTERNATIVE GATE DIELECTRIC APPLICATION. Wen-Jie Qi, Keith Zawadzki, Renee Nieh, Yongjoo Jeon, Byoung Hun Lee, Aaron Lucas, Laegu Kang and Jack C. Lee, Microelectronics Research Center, The University of Texas at Austin, Austin, TX.

Hysteresis effect of barium strontium titanate thin films for gate dielectric application has been studied. The hysteresis was measured using HP 4194 and the charge trapping property was measured using HP 4156. It is found that the "counterclockwise" hysteresis has strong sweep voltage dependence and operating temperature dependence. It can be reduced or eliminated by proper thermal annealing or by using a barrier layer. A charge trapping and detrapping mechanism has been proposed.

**NN7.2**

PANTADIONATE: AN ALTERNATE SOL-GEL ROUTE TO SYNTHESIS OF FERROELECTRIC Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> (x=0.2, 0.4, 0.6). Pramod K. Sharma<sup>1</sup>, G.J. Moore<sup>2</sup>, K.A. Jose<sup>1</sup>, V.V. Varadan<sup>1</sup> and V.K. Varadan<sup>1</sup>. <sup>1</sup>Research Center for the Engineering of Electronics and Acoustic Materials, Department of Engineering Science and Mechanics, The Pennsylvania State University, University Park, PA, <sup>2</sup>Materials Research Center, Department of Chemistry, SUNY at Binghamton, New York, NY.

Sol-gel synthesis of transitional metal oxides is one of the important technique to obtain the pure and homogenous materials at low temperature. In this work, Barium strontium titanate (BST) was synthesized by sol-gel processing using pentadionate as the precursors of metal oxides. The Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> was prepared for three values of x i.e. 0.2, 0.4 and 0.6. The obtained powders were heated from 500 C to 1200 C at the interval of 200 C to determine the temperature of crystallization. The phase of the final products was investigated by X-ray diffraction (XRD). The effect of temperature on the weight loss of the xerogel was understood by Thermal gravimetric analysis [TGA]. Two kinds of particle size (<100 nm and 200-400 nm) were observed under the Scanning electron microscope (SEM) of the heat treated xerogels. It is important to note that powders with the nano/submicrons size have improved properties. The dielectric properties were determined by impedance analyzer in the frequency range from 1KHz to 1MHz and explained in detail for the different values of x.

**NN7.3**

CRYSTALLIZATION KINETICS OF BARIUM-MAGNESIUM NIOBATES FROM HYDROTHERMALLY TREATED PRE-CURSORS. Anderson Dias, Paulo Ernesto Freiheit Cortes, Margaret Spangler Andrade, Fundao Centro Tecnol6gico de Minas Gerais-CETEC, Setor de Tecnologia Metallurgica, Belo Horizonte-MG, BRAZIL.

Differential Scanning Calorimetry is a thermal analysis technique for the measurement of temperatures and heat flows associated with transitions in materials. In the present work, a differential scanning calorimeter was employed to extract quantitative and qualitative information about physical and chemical changes involved during heating of partially crystallized barium magnesium niobate (BMN) powders, obtained from hydrothermally treated precursors.

Conventional preparation techniques of these materials involve several firing steps at high temperatures, leading to crystalline but hard agglomerated powders, which difficult the final step (sintering). On the other hand, a soft solution process, like the hydrothermal method, is a well-known environmentally friendly process, producing nanometric and reactive powders at low temperatures and pressures. Hydrothermal treatments on barium, magnesium and niobium salts were conducted at 473K, for 4 hours, under saturated vapor pressure. X-ray diffraction, X-ray fluore

#### NN7.4

**THERMODYNAMICAL MODELING, HYDROTHERMAL SYNTHESIS AND ATOMIC FORCE MICROSCOPY CHARACTERIZATION OF LEAD ZIRCONATES.** Anderson Dias, Margareth Spangler Andrade, Setor de Tecnologia Metalrgica, Fundao Centro Tecnol6gico de Minas Gerais, Belo Horizonte-MG, BRAZIL; Virginia Sampaio Teixeira Ciminelli, Depto. Engenharia Metallurgica e de Materiais, UFMG, Rua Espirito Santo, Belo Horizonte-MG, BRAZIL.

Hydrothermal processing involves several simultaneous reactions between chemical species in an aqueous system to produce inorganic materials at significantly lower temperatures and pressures. These lower temperatures for the preparation of multi-component oxides affect the energy consumption, which is strongly related to environmental pollution. Thus, synthesis methods that do not require high energy or are conducted under environmentally benign conditions are the most promising technological routes for the production of electroceramics. In the present work, the hydrothermal processing conditions of lead zirconate powders were studied by using a thermodynamic model of electrolytic solutions in order to avoid the empirical trial-and-error mode of synthesis. The approach used makes possible to predict the optimum conditions through stability and yield diagrams, relating the equilibrium concentration of all the present species as a function of temperature, pressure, solution pH and input reagent concentrations.

#### NN7.5

**EPITAXIAL GROWTH OF  $Sr_{0.3}Ba_{0.7}Nb_2O_6$  THIN FILMS PREPARED BY SOL-GEL PROCESS.** Keishi Nishio, Jirawat Thongrueng, Yuichi Watanabe and Toshio Tsuchiya, Science Univ of Tokyo, Dept of Materials Science and Technology, Chiba, JAPAN.

We succeeded in the preparation of strontium-barium niobate ( $Sr_{0.3}Ba_{0.7}Nb_2O_6$ : SBN30) that have a tetragonal tungsten bronze type structure thin films on  $SrTiO_3$  (100), STO, or La doped  $SrTiO_3$  (100), LSTO, single crystal substrates by a spin coating process. LSTO substrate can be used for electrode. A homogeneous coating solution was prepared with Sr and Ba acetates and Nb(OEt)<sub>5</sub> as raw materials, and acetic acid and diethylene glycol monomethyl ether as solvents. The coating thin films were dried at 200°C or 400°C for 1h and sintered at temperature from 700°C to 1000°C for 6h in air. SBN30 crystallized at temperature above 700°C. A grain shape of the thin film on STO or LSTO substrate was columnar. These columnar-shaped grains were aligned right angle each other. A mean grain size of the film on STO was larger than that on LSTO. It was confirmed that the thin films sintered above 700°C were in the epitaxial growth because the 16 diffraction spots were observed on the pole figure using (121) reflection. The  $\langle 130 \rangle$  and  $\langle 310 \rangle$  direction of the thin film on STO were oriented with the c-axis in parallel to the substrate surface. The oriented direction of the thin films prepared on LSTO have not been clarified. The thin films on LSTO sintered at 1000°C showed  $P - E$  hysteresis loop.

#### NN7.6

**NEAR-STOICHIOMETRIC BARIUM TITANATE SYNTHESIS BY LOW TEMPERATURE HYDROTHERMAL REACTION.** Kyoungja Woo, Guang J. Choi, Young S. Cho, Korea Institute of Science and Technology, Clean Technology Research Center, Seoul, KOREA.

Barium-deficiency of barium titanate particles prepared by low temperature hydrothermal reaction has been notorious. It has been believed that barium-deficiency is caused by the high solubility of barium source compared with titanium. Here is reported the synthesis of near-stoichiometric barium titanate powders with ultrafine particle size and high crystallinity by low temperature hydrothermal reaction from barium acetate and titanium tetra(methoxyethoxide). Barium titanate particles were synthesized in the spherical, metastable cubic crystalline grains with size distribution between 60-90 nm in diameter. Ultrafine particle size was resulted from the control of the hydration rate and the decrease of Ti-O-Ti cross-linking extent of titanium precursor. Increasing barium to titanium molar ratio in reactant could not overcome the notorious barium-deficiency but, improved stoichiometry and produced finer and less agglomerated particles. Interestingly, adding a slight pressure to autogeneous one to make total 4-10 atm has yielded near-stoichiometric, highly crystalline, and less agglomerated barium titanate particles. It seems like that the

total pressure around 4-10 atm provides strong force enough to push barium ions into the interstitial points of perovskite structure and stabilize it. These particles, which were in metastable cubic form as synthesized, initiated phase transition to tetragonal form by calcination at below 400 degree Celsius.

SESSION NN8: POSTER SESSION:  
BATTERIES AND FUEL CELLS  
Chair: Anthony C. Jones  
Tuesday Evening, November 30, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### NN8.1

**DIRECT FABRICATION OF  $LiCoO_2$  FILM ELECTRODES USING SOFT SOLUTION-PROCESSING IN  $LiOH$  SOLUTION AT 20-200°C.** Masahiro Yoshimura, Seung-Wan Song, Kyoo-Seung Han, Tokyo Institute of Technology, Center for Materials Design, Materials and Structures Laboratory, Yokohama, JAPAN.

Application of Soft Solution-Processing, which is defined by environmentally friendly processing using (aqueous) solution, to the field of lithium batteries has been demonstrated by fabricating lithium cobalt oxide film on the cobalt metal substrate in  $LiOH$  solution under hydrothermal condition. The film fabrication can be interpreted in terms of chemical dissolution of cobalt plate in  $LiOH$  solution at fixed temperature between 20 and 200°C resulting in the formation of  $H_{1-n}CoO_2$  where n value increases with reaction temperature, and heterogeneous nucleation by reacting with  $Li^+$  ions followed by crystal growth. The crystal structure was confirmed by X-ray diffraction, X-ray photoelectron and microRaman spectroscopy. According to X-ray diffraction and scanning electron microscopic analyses, the films show a good crystallinity despite the low reaction temperature without any post synthesis annealing. The films prepared under different conditions show different phase selection such as spinel (Fd3m) or hexagonal (R3-m), surface morphology and film thickness. An electrochemical activity of the lithium cobalt oxide films was evidenced from cyclic voltammogram, since redox peak potentials are similar to those of powder electrode.

#### NN8.2

**THE GROWTH AND MICROSTRUCTURE ANALYSIS OF NEW PIEZOELECTRIC MATERIAL ( $La_3Ga_5SiO_{14}$ ).** Il Hyoung Jung, Keun Ho Auh, Ceramic Processing Research Center, Hanyang University, Seoul, KOREA.

$La_3Ga_5SiO_{14}$  is a new piezoelectric material which was determined from its acoustic characteristics. In this experiment,  $La_3Ga_5SiO_{14}$  single crystals were successfully grown by the self-designed Czochralski system. We confirmed that  $La_3Ga_5SiO_{14}$  has higher electromechanical coupling coefficient and much less acoustic loss than quartz and  $LiTaO_3$ . And also, in order to improve the piezoelectric characteristics, we investigated for the microstructure and defect of grown crystals. From the above results, we will demonstrate for the ability of improving piezoelectric characteristics through the analysis of grown crystals.

#### NN8.3

**EFFECT OF P2O5 CONTENT ON PROTON CONDUCTIVITY OF AMORPHOUS ZIRCONIUM PHOSPHATE THIN FILMS.** Yong-il Park and Masayuki Nagai, Department of Energy Science and Technology, Musashi Institute of Technology, Setagaya-ku, Tokyo, JAPAN.

Amorphous zirconium phosphate thin films of various composition  $xZrO_2 \cdot (1-x)P_2O_5$  were fabricated on glass substrates and Pt/Si wafers by sol-gel spin coating for low-temperature fuel cell application. A large increase of electrical conductivity was observed in the obtained thin films with increasing P2O5 content. Effects of heat-treatment temperature and humidity on electrical conductivity and chemical stability of the thin films were investigated.

#### NN8.4

**EFFECT OF PRECURSOR SOL AGEING ON SOL-GEL DERIVED RUTHENIUM OXIDE THIN FILMS.** S. Bhaskar, S.B. Majumder, P.S. Dabal and R.S. Katiyar, Department of Physics, University of Puerto Rico, San Juan, PR; Angel L. Morales Cruz and Estevao Rosim Fachini, Dept of Chemistry, University of Puerto Rico, San Juan, PR.

Ruthenium Oxide ( $RuO_2$ ) thin films for the use as bottom electrode, were prepared by sol-gel technique using  $RuCl_3 \cdot xH_2O$  as the precursor material. Multi layer coatings deposited by spin coating onto Si substrates were 0.8µm thick. Films were heat treated at 300, 400, 500, 600 and 700°C to study the effect of annealing temperature on conductivity and microstructure. Samples fired at 300°C were

amorphous and all others were polycrystalline in nature. Room temperature measurements indicate that the resistivity decreased with increasing the firing temperature and it was least for the sample fired at 700°C of 3.33  $\mu\Omega$ -m. A comparative study of RuO<sub>2</sub> thin films, of freshly prepared sol and those aged' for extended period of time in ambient air was carried out by XRD, AFM and XPS techniques. The conductivity measurements were carried out to characterize morphological and compositional changes. Aged' films indicate very poor conductivity and ageing of the sol is believed to affect the crystallinity and orientation of the growth of RuO<sub>2</sub> films. Surface morphology of the freshly prepared sol has uniform and dense microstructure and the other set of samples has microcracks and poor uniformity. XPS analysis indicates that the ruthenium chemical state and the oxygen content in the films, could explain the observed changes in conductivity and microstructure of these films. This work was supported in part by DAAG55-98-1-0012 and DE-FG02-91ER 75764 grants.

#### NN8.5

A STUDY OF SURFACE EXCHANGE COEFFICIENT ON La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub> THIN FILMS. X. Chen, SVEC and MRSEC, University of Houston, Houston, TX; S. Wang, Y.L. Yang, Department of Chemistry and MRSEC, University of Houston, Houston, TX; L. Smith, N.J. Wu, SVEC and MRSEC, University of Houston, Houston, TX; A. Jacobson, Department of Chemistry and MRSEC, University of Houston, Houston, TX; A. Ignatiev, SVEC and MRSEC, University of Houston, Houston, TX.

La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub> (LSCO) can be used as an important cathode material for solid oxide fuel cell applications. LSCO epitaxial thin films have been deposited on LaAlO<sub>3</sub> substrates by pulsed laser deposition. The sample was heated to high temperatures, and subjected to abrupt oxygen partial pressure changes. The transient behavior of the thin film conductivity with the pressure changes was recorded. The surface exchange coefficient *k* of the LSCO thin film was obtained from such electrical conductivity relaxation analysis. The measured surface exchange coefficient increases with temperature and with final pressure under pressure switching, but is not sensitive to the initial pressure. After prolonged annealing at 900°C, the *k* value was found to have greatly increased. The reason for the change of the thin film surface exchange coefficient with the prolonged annealing is discussed.

#### SESSION NN9: POSTER SESSION: SiC

Chair: Anthony C. Jones  
Tuesday Evening, November 30, 1999  
8:00 P.M.  
Exhibition Hall D (H)

#### NN9.1

CVD OF SiC FROM METHYLSILANE: INFLUENCE OF REACTION SURFACE TO VOLUME RATIO ON GROWTH KINETICS AND DEPOSIT STRUCTURE. Andrei M. Abyzov, Yuri V. Mahov, Evgenii P. Smirnov, State Institute of Technology, St.-Petersburg, RUSSIA.

The chemical vapor deposition of silicon carbide from methylsilane (MS) — hydrogen mixture (molar ratio MS:H<sub>2</sub>=1:30) at 700...800°C was studied in a low-pressure ( $\approx 1$  kPa) isothermal hot-wall reactor. Depending on the reaction surface to volume ratio S/V and mass-transfer conditions experiments of 3 types were made. (i) Substrates being silicon plates or graphite rods placed immediately in the reactor's tube (S/V=3 cm<sup>-1</sup>), the growth rate has maximum values (2 mg/(cm<sup>2</sup>·h) at 800°C) and the activation energy E is 235 kJ/mol. (ii) Substrates being silicon plates inserted into the slit cavity or graphite rods enclosed in the tube cavity (S/V=20 cm<sup>-1</sup> or 40 cm<sup>-1</sup>), the reaction space is a "macropore" with the equivalent diameter  $d_e=4/(S/V)=1...2$  mm, the deposition rate decreases in 2...4 fold and the activation energy remains nearly the same — 250 kJ/mol. (iii) Carbon fiber of 0,7 mm diameter being strained along reactor's axis, SiC is deposited onto filaments of 7  $\mu$ m diameter ("micropore" reaction space, S/V=6 · 10<sup>3</sup> cm<sup>-1</sup>), the deposition rate has minimum values and E=250 kJ/mol again. Calculation based on Nusselt number (i) or Thiele modulus (ii, iii) indicates that diffusion limitation with respect to initial reactant — MS — is absent (kinetic control).  $d_e \gg \lambda$  for the (i, ii) reaction geometry,  $d_e \approx \lambda$  for the (iii) one, where  $\lambda \approx 6 \mu$ m — a mean free path of MS molecules. According to XPS layers deposited (i, ii) are nearly stoichiometric (Si:C $\approx$ 1,2), hydrogen content [H]  $\leq 1\%$  (at.) according to IR-transmission spectra. On the basis of XRD the structure of SiC deposit varies from amorphous (i) to polycrystalline (iii). Data obtained indicates a multi-step process: (a) active intermediate (probably methylsilylene biradical) formation from MS in a gas phase; (b) relaxation of SiC growing from amorphous to crystalline state that had no time to

occur at high deposition rates CH<sub>3</sub>SiH<sub>3</sub> (g) → CH<sub>3</sub>SiH (g) → a-SiC (s) → c-SiC (s).

#### NN9.2

CRYSTALLOGRAPHIC ORIENTATION IN BULK POLY-CRYSTALLINE SILICON CARBIDE PRODUCED BY A CHEMICAL VAPOR DEPOSITION (CVD) PROCESS. James V. Marzik, Performance Materials, Inc., Hudson, NH; William J. Croft, Mineralogical Museum, Harvard University, Cambridge, MA.

Polycrystalline, theoretically dense silicon carbide was deposited onto graphite substrates via the reductive pyrolysis of methyltrichlorosilane in a hot-walled chemical vapor deposition (CVD) chamber. The resulting product can be considered a bulk material with deposit thicknesses in the range of 4 to 8 millimeters. The material was characterized using powder x-ray diffraction and Laue back-reflection techniques. Under the deposition conditions investigated in this study, the crystallographic orientation varied as a function of distance from the substrate. The material exhibited a high degree of randomness in proximity to the substrate, and progressively showed a higher degree of preferred crystallographic orientation as the deposit progressed. This phenomenon is correlated with the microstructure of the material as well as such mechanical properties as hardness and fracture toughness.

#### NN9.3

Abstract Withdrawn.

#### SESSION NN10: CERAMICS

Chair: Reid F. Cooper  
Wednesday Morning, December 1, 1999  
Room 312 (H)

#### 8:45 AM NN10.1

STRUCTURE-PROPERTY RELATIONS IN SOL-COATED PMN CERAMICS: MICROSCOPY, DIELECTRIC AND ELECTRO-MECHANICAL RESPONSE. Alp Sehrioglu, S.M. Pilgrim, New York State College of Ceramics at Alfred University, Alfred, NY.

Some of the most promising materials for electrostrictive response are PMN ceramics; however, the properties of a given composition are only optimum in a limited range of temperatures. In a previous study, it was found that sol coating of PMN particles modified and improved the electromechanical and/or dielectric properties of the resulting product—doubling induced strain in some cases. Understanding the origin of these changes will help to produce an optimized PMN ceramic for a given application from a single source powder. This work concentrates on the Ti and Zn coatings which gave superior properties within the concentration matrix. In this case, a second phase, containing Zn and Mg, is found at the triple points of the sintered body. The relation between the formation of the second phase and the enhanced electrostrictive behavior is studied. Complete characterization of the system by XRD, TEM, SEM clarifies the response. Electrical measurements of dielectric constant, loss, polarization, strain and conductivity provide the property determinations needed to complete the structure-property suite. Funding acknowledgement: ONR N00014-96-1-0961.

#### 9:00 AM NN10.2

THE CONTROL OF Zn FOR ZST MICROWAVE CERAMICS WITH LOW SINTERING TEMPERATURE. Yong H. Park, Moo Y. Shin, Ji M. Ryu, Kyung H. Ko, Ajou Univ, Dept of Material Science and Engineering, Suwon, KOREA.

ZnO have been a potential additives for sintering of Zirconium Titanate Tin Oxide at low T( $\leq 1400^\circ\text{C}$ ). But it also has serious side effects such as decrease of Qxf value. In this work, the curing of these side effects on the dielectric properties of ZST without any further chemical additives will be presented. ZST ceramics were prepared via conventional method and their microwave dielectric properties including quality factor, permittivity and temperature coefficient of resonant frequency (TCF) were measured at X-band. After sintered at 1350<sup>±</sup>10°C, samples were annealed in air and oxygen at 900~1100°C for 5hr. It was observed that among specimens, Qxf value of ZST annealed at 900°C increased from the as-sintered value to 46000 without any sacrifices of other dielectric properties such as dielectric constant and TCF. From XRD and microscopic analysis, there were no formations of second phases and insignificant changes in lattice constants which could affect microwave properties of ZST. However, it was found that only for the specimens annealed at 900°C, all of Zn contents was not detected inside of grain, but in grain boundary. So, it is suggested that the out-diffusion of Zn is responsible the increase of Qxf value. As another preparation technique of ZST, the mixed powders containing ZnO were pre-pressed, then put into calcination and sintering successively. The ZST could be sintered at as low as

1250°C, but with poor  $Q \times f$  value. After annealing at 900°C, the recovery of  $Q \times f$  value up to  $\sim 40000$  was observed with same Zn distribution profile as previous experiment.

#### 9:15 AM NN10.3

CHEMICAL VAPOR DEPOSITION OF CONFORMAL ALUMINA THIN FILMS. Bradley D. Fahlman and Andrew R. Barron, Department of Chemistry, Rice University, Houston, TX.

Deposition onto ZnS particles was carried out using  $\text{AlH}_3(\text{NMe}_2\text{Et})$  and water vapor as co-precursors within a fluidized-bed reactor. Silver nitrate and lead acetate tests, as well as SEM/microprobe analyses confirmed the presence of a conformal coating of alumina. Deposition onto silicon wafers, quartz and carbon fibers were also carried out utilizing the same precursors within a hot-wall APCVD apparatus. Growth rates were on the order of 40-80 Å/min at 165°C. Films were characterized by SEM, microprobe and X-ray diffraction. The conformality of the films was illustrated using silicon wafers that were etched prior to deposition. In all cases, the films consisted of pure amorphous alumina, possessing less than 3 wt% carbon.

### SESSION NN11: SiC & DIAMONDS

Chair: Reid F. Cooper

Wednesday Morning, December 1, 1999  
Room 312 (H)

#### 10:00 AM NN11.1

GROWTH OF SILICON CARBON NITRIDE FILMS USING METHYLAMINE IN AN ELECTRON CYCLOTRON RESONANCE PLASMA CHEMICAL VAPOR DEPOSITION REACTOR. J.-J. Wu, K.H. Chen, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, TAIWAN; C.-Y. Wen, L.C. Chen, Center for Condensed Matter Sciences, National Taiwan University, Taipei, TAIWAN; H.J. Lo, S.T. Lin, Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei, TAIWAN; Y.C. Yu, C.W. Wang, E.K. Lin, Institute of Physics, Academia Sinica, Taipei, TAIWAN.

Ternary SiCN phases are attractive because of their potential for fast-speed electronic as well as blue and UV optoelectronic applications. In our previous work, we have demonstrated that the process of SiCN by electron cyclotron resonance plasma chemical vapor deposition possesses potential in facilitating SiCN nucleation. Continuous polycrystalline SiCN films with high nucleation density have been successfully deposited by this method. However, no carbon incorporation into the SiCN films deposited using  $\text{CH}_4$  without  $\text{H}_2$  addition by ECR plasma CVD was observed.  $\text{H}_2$  addition was found to increase the concentrations of the active carbon species in the gas phase through hydrogen abstraction reactions. In order to enhance further the carbon content within the films, methylamine ( $\text{CH}_3\text{NH}_2$ ) were used to synthesize the SiCN films in this study. From the view point of kinetics, the rate constant of  $\text{CH}_3\text{NH}_2$  dissociation reaction is 8 orders of magnitudes higher than that of  $\text{CH}_4$  dissociation reaction at 1000K. Using  $\text{CH}_3\text{NH}_2$  as carbon source could provide more abundant active carbon species in the gas phase to enhance the carbon incorporation within the SiCN films. Primary results show that SiCN film was deposited successfully without  $\text{H}_2$  addition during the film growth. The growth characteristics and some optical and electronic properties of the SiCN films deposited using methylamine will be discussed.

#### 10:15 AM NN11.2

INTERACTIONS OF OXYGEN WITH 4H- AND 6H-SiC. Y. Song and F.W. Smith, Physics Dept., City College of New York, NY.

The ability to grow passivating  $\text{SiO}_2$  surface coatings on SiC is an important advantage of this material in both electronic and ceramic applications. The  $\text{SiC} + \text{O}_2$  reaction leading to the formation of  $\text{SiO}_2$  is complicated, however, by presence of carbon and by the need to remove it as a gaseous product. The predictions of thermodynamic calculations of the possible vapor ( $\text{SiO}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ) and solid phase ( $\text{SiC}$ ,  $\text{SiO}_2$ , C, Si) components and their locations in a CVD phase diagram will be presented and discussed. At high T and low  $\text{O}_2$  pressures,  $\text{P}(\text{O}_2)$ , the SiC surface is etched, with the volatile SiO and CO species being formed. At intermediate T and  $\text{P}(\text{O}_2)$  the products are  $\text{SiO}_2$  and CO, while at low T and high  $\text{P}(\text{O}_2)$  only solid products are predicted to be formed, i.e.  $\text{SiO}_2$  and C. The unexpected prediction that solid C is a thermodynamically-stable product of the interaction of oxygen with SiC at low temperatures and high  $\text{O}_2$  pressures will be analyzed and its implications for the growth of passivating  $\text{SiO}_2$  films on SiC will be discussed. Finally, experimental investigations of the interactions of oxygen with Si- and C-terminated (0001) surfaces of 4H- and 6H-SiC and of the resulting products will be presented.

#### 10:30 AM NN11.3

SURFACE CHEMISTRY OF OXYGENATED, HYDROGENATED AND HALOGEN TREATED LOW INDEX DIAMOND SINGLE CRYSTAL SURFACES. Carsten Benndorf, Sven Hadenfeldt, University of Hamburg, Department of Physical Chemistry, Hamburg, GERMANY.

Processes, such as chemisorption and reaction at diamond surfaces are believed to play an important role in low-temperature diamond growth. The investigation of such processes can lead to a better understanding of the underlying growth mechanisms. The lowering of the substrate temperature achieved by using halogenated precursors is thought to involve surface processes, such as halogen adsorption, desorption and reaction with H(ad). In the present work we examined oxygenated and hydrogenated low index diamond (100), (111) and (110) single crystal surfaces, as well as polycrystalline diamond CVD films in UHV. The surfaces and their interactions with fluorine and chlorine were studied, using thermal desorption mass spectroscopy (TDS), Augerelectron spectroscopy (AES), low energy electron diffraction (LEED) and photoelectron spectroscopy (UPS / XPS). Hydrogenation was accomplished by ex situ treatment in a hydrogen plasma, oxygenation by chemical means as well as using an oxygen containing plasma. Elemental halogen was dosed by direct dosing of chlorine gas through a heated oxide ceramics tube or by solid state electrolysis of the halogenchloride at elevated temperatures. Depending on the sample preparation and history, in general two different desorption behaviours are observed in TDS. From the hydrogen rich, plasma prepared surface chlorine is desorbed continuously with a maximum around 600 K, and being completely removed around 850 K. On a hydrogen depleted surface, where less halogen adsorbs at a given exposure, two regions of chlorine desorption are observed. Up to 730 K a steady decrease of chlorine is noted, levelling off, until finally all chlorine is desorbed around 950 K. Halogen uptake of the diamond surface can be increased either by thermally activating the surface or by dosing of atomic hydrogen prior to halogen adsorption. UPS and XPS results clearly show differences between various sorts of surface pretreatment and surface reaction.

#### 10:45 AM NN11.4

GRAIN BOUNDARY EFFECTS ON CURRENT TRANSPORT IN MICROBRIDGES OF B-DOPED HIGHLY ORIENTED DIAMOND. Dierk Steinbach, Andre Flöter, Michèle Hirsch, Herbert Güttler, Paul Ziemann, Daimler Chrysler Forschung und Technologie, Ulm, GERMANY.

Large area highly oriented diamond (HOD) films grown by chemical vapor deposition (CVD) on silicon substrates are economically important in replacing single crystal diamond as a material for active electronic devices. In order to optimize device characteristics it is crucial to understand the influence of grain boundaries on current transport. For this purpose, the effect of the presence and orientation of grain boundaries on electrical transport properties is studied by measuring the electrical conductivity on a micrometer scale including measurements on single grain boundaries. The latter are enabled by patterning  $10^{18} \text{ cm}^{-3}$  B-doped HOD films (N-concentration  $4.5 \cdot 10^{17} \text{ cm}^{-3}$  as determined by SIMS) grown on HOD films resulting in microbridges as narrow as  $3.5 \mu\text{m}$ . Four probe electrical measurements are performed in a temperature range from 22°C to 27°C and applying fields up to 0.2 MV/cm. Additionally, the grain structure and phase purity is characterized using SEM, Raman and Auger spectroscopy. From the electrical measurements we find that the conductivity for  $V = 0\text{V}$  at 22°C is  $6.4 \cdot 10^{-4} \text{ 1}/\Omega\text{cm}$  for a bridge containing no grain boundary. For bridges with a grain boundary perpendicular to current flow the conductivity is reduced by a factor 3/2, whereas for bridges with a grain boundary parallel to current flow the conductivity is increased by a factor 2. The temperature dependence of the electrical conductivity for zero voltage reveals a single activation energy. For samples without a grain boundary as well as with a perpendicular grain boundary this activation energy is 330 meV. However, for a bridge with a parallel grain boundary we find a reduced activation energy of 280 meV. At higher voltages the current voltage characteristics are more complex and affected by ohmic heating. The results of the electrical measurements will be presented and discussed with respect to structural properties.

### SESSION NN12: POLYMERS

Chair: Reid F. Cooper

Wednesday Morning, December 1, 1999  
Room 312 (H)

#### 11:00 AM NN12.1

PHYSICO-CHEMICAL ANALYSIS OF POLYMER INSULATOR MATERIAL SUBJECTED TO ACID RAIN CONDITION. Ramanujam Sarathi, Indian Institute of Technology, Department of Electrical Engineering, Chennai, INDIA; R. Vijayaraghavan, Indian

Institute of Technology, Materials Science Research Centre, Chennai, INDIA; P. Umashankar, Indian Institute of Technology, Department of Electrical Engineering, Chennai, INDIA.

Polymer materials are currently being used as outdoor insulator for high voltage power transmission and in distribution lines because of their better dielectric properties, light weight and economic benefit compared to the porcelain insulator. When selecting the insulators, there are choices that encompasses both material properties and design. The performance of insulators identifies by many means and it has been identified earlier, the most of the failure is due to the Tracking Phenomena. Tracking is by Definition, is the formation of a permanent conducting path across the surface of the insulator. With the Advancement of Power transmission capacity, it has become necessary to design and develop a reliable, compact and cost effective insulation system. These days the DC power transmission is growing tremendously because of its own advantages. Earlier much work has been carried out to understand the tracking phenomena under AC voltages and the data available under the DC voltages are scanty. In addition, with the tremendous growth of industries, the world over, pollution is one of the major drawback causing acid rain in many locations of the industrial belt. The major composition of the acid rain being the sulphuric acid, nitric acid and oxalic acid. Having known all this, in the present work, to obtain a complete database, a methodical experimental run has been carried out following the IEC-587 standards, to understand the tracking phenomena especially under the DC voltages, with HDPE (high density poly ethylene, the ideal insulation material for DC system) aged under different condition Viz. corona ageing, samples aged under different acid solutions ( nitric acid, sulphuric acid and oxalic acid). To understand the morphological changes in the tracking formed zone of the material, physico-chemical analysis has been carried out using WAXD, DSC, FTIR and EPR. The important conclusions obtained based on the present work are the following 1. Tracking phenomena is much severe under positive DC voltages. 2. Erosion of the materials observed due to ageing of the samples in acid solution and the severity is much with the sulphuric acid compared to oxalic acid and nitric acid. 3. WAXD results indicates no addition of phase in the material due to tracking. 4. DSC results indicates a reduction in enthalpy in the tracking formed zone. 5. EPR results shows presence of Free radicals in the tracking formed zone. Degradation mechanism has been enlightened. 6. Formation of aldehydes and ketones in HDPE material due to tracking identified using the FTIR analysis, is the indication that the tracking is a damage generating process. The other important results as and when accrued before the submission of the final version will be included to the conference.

**11:15 AM NN12.2**

**PULSED PLASMA ASSISTED CVD OF SUPER HYDROPHOBIC FLUOROCARBON SURFACES.** HaiBo Qiu, Univ. of Texas at Arlington, Materials Science and Engineering Program; Richard B. Timmons, Univ. of Texas at Arlington, Chemistry and Biochemistry Dept, Arlington, TX.

Super hydrophobic polymeric surfaces were successfully prepared by variable duty cycle pulsed plasma polymerization of saturated fluorocarbon monomers. The hydrophobic nature of these films was studied as functions of processing variables, particularly peak power inputs and plasma duty cycles. By careful adjustment of these variables, it is possible to synthesize films having sessile contact angle in excess of 170°. The super hydrophobic surfaces are more a result of morphological factors than unusual chemical compositions. A high level of tunability of the physical and chemical structures of these samples is achievable via systematic variations of key plasma variables. Variation in the surface morphology, wettability and important physical properties, such as dielectric constants, with changes in film formation conditions will be presented.

**11:30 AM NN12.3**

Abstract Withdrawn.