# SYMPOSIUM F

## Transport and Microstructural Phenomena in Oxide Electronics

April 16 – 20, 2001

### Chairs

**Dave H.A. Blank**
MESA
Univ of Twente
MASIF
Enschede, 7500 AE NETHERLANDS
31-53-4893121

**David S. Ginley**
Natl Renewable Energy Lab
SERF W102
Golden, CO 80401
303-384-6573

**Marilyn E. Hawley**
Los Alamos National Laboratory
MS G755 MST 8
Los Alamos, NM 87545
505-665-3600

**Stephen K. Streiffer**
Materials Science Division
Argonne Natl Lab
Bldg 212 C212
Argonne, IL 60439-4838
630-252-5832

**David C. Paine**
Div of Engineering
Brown Univ
182 Hope St
Providence, RI 02912
401-863-1457

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* Invited paper

# TUTORIAL

**ST F: ADVANCED DEPOSITION AND CHARACTERIZATION TECHNIQUES**
**Monday, April 16, 2001**
**1:30 p.m. - 5:00 p.m.**
**Salon 3/4 (Marriott)**

This tutorial will include lectures on three advanced deposition techniques and one lecture on in-situ characterization methods for the fabrication of high quality epitaxial oxide films. The tutorial will include in-depth descriptions of three particular growth techniques (Pulsed Layer Deposition (PLD), Atomic Layer Epitaxy (ALE), and Combinatorial Deposition). The tutorial will conclude with a lecture focused primarily on X-RAY film characterization. Each of the four segments will include background information, a description of the respective method, the current state-of-the-art, and unique advantages and limitations, e.g. fabrication of a specific oxide film, achievement of surface smoothness, versatility, rapid compositional evaluation, or integration in multistep hybrid device fabrication schemes. The intention of the short course is to introduce the attendee to background and overview information on each of these deposition methods and the use of X-RAY diffraction techniques to assess film quality and crystallographic growth orientation.

**Instructors:**
**Ichiro Takeuchi**, University of Maryland
**Thomas E. Seidel**, Genus, Inc.
**Quanxi Jia**, Los Alamos National Laboratory
**Darrell Schlom**, The Pennsylvania State University

SESSION F1: TRANSPARENT CONDUCTING OXIDES I
Chairs: David S. Ginley and Hiroshi Kawazoe
Tuesday Morning, April 17, 2001
Salon 3/4 (Marriott)

**8:30 AM *F1.1**
MATERIALS ISSUES IN THE SCIENCE AND TECHNOLOGY OF TCO. Hiroshi Kawazoe, HOYA Corp., R&D Center, Tokyo, JAPAN.

In the present paper our recent approaches to several problems in the science and technology of TCO will be discussed. The first topic concerns p-type conducting wide gap oxides such as CAO, CGO, and SCO. Discussed will be chemical design of the oxides from the viewpoints of electronic structures and crystal structures, fabrication and optoelectronic properties of the thin films, diode functions of the heterojunctions produced by using the newly found oxide as a p-type material, and the very new results of an extension of the chemical design to oxysulfides. The second topic is the fabrication of the ITO thin films with very low resistivity. Hetero-epitaxial thin films of ITO were grown on a single crystalline YSZ substrate by PLD. The thin film obtained was not a perfect single crystalline film, but density of grain boundaries was greatly reduced. The maximum and reproducible conductivity was 1.3 x $10^4$Scm−1. The high conductivity was derived from relatively high Hall mobility of 42 $cm^2V-1s-1$. The results obtained are very reproducible. The remaining major problem is developments of fabrication techniques suitable for the high quality thin films. In the last topic discussed will be fabrication and some optoelectronic functions of amorphous TCO materials. Low temperature deposition of TCO thin films on plastic films is one of important technological problems. The deposition usually gives rise to amorphous thin films. Therefore, finding of new amorphous TCO materials with high conductivity is expected. Some examples are shown with particular reference to the relationship between chemical composition and properties of the materials.

**9:00 AM *F1.2**
TRANSPARENT CONDUCTIVE OXIDE SEIMCONDUCTOR ZnO:Al FILMS PRODUCED BY MAGNETRON REACTIVE SPUTTERING. M. Chen, J. Chen, Y.H. Yu, X. Wang, Ion Beam Laboratory, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai, CHINA; Z.L. Pei, C. Sun, L.S. Wen, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, CHINA.

Fabrication of as low as possible resistivity with retaining high transparency in visible region is the aim of many works having been done on TCO films. Sn-doped $In_2O_3$ is the predominant commercial TCO films, but recently, ZnO:Al ZAO is emerging as an alternative to ITO, not only due to their comparable electrical properties, but also its cost-effective {a cheap, abundant and no-toxic material, easily fabrication}, furthermore, good stability in hydrogen plasma, which is of significance for applications related to amorphous silicon solar cell, etc. In this work, the structural, electrical and optical properties of ZnO:Al films deposited on quartz glass substrates by using dc magnetron reactive sputtering from a Zn target mixed with Al were studied. The Al enrichment on the film surface was observed. It was also observed that the {002} peak position of all films shifts to lower angle comparable to that of bulk ZnO due to the residual stress change with deposition parameters. The increase of carrier concentration and Hall mobility with substrate temperature increases was due to the out-diffusion of absorbed oxygen content, the improvement of crystalline and the free of residual stress, while the decrease of Hall mobility at the substrate temperature of 350°C was attributed to the composition deviation and residual stress increases. The optimum substrate temperature is about 240°C that is 100°C lower than the one to deposit ITO films. On the other hand, the dependence of electrical properties on Al doping content indicates that the increase of carrier concentration was due to the Al doping content increase but the increase of Hall mobility was due to the residual stress decrease. The minimum resistivity is 4.23E$10^{-4}\Omega$·cm with a carrier concentration of 9.21E20 $cm^3$ and Hall mobility of 16.0 $cm^2\ v^{-1}s^{-1}$. The visible transmittance of over 80% and infrared reflectance of about 80% were obtained. The infrared reflectance in the range of 2.5 to 25 mm increases with sheet resistance decrease. The optical band gap widening was ascribed to the Burstein-Moss effect. In general, the study indicates that ZAO films show comparable electrical and optical properties with that of ITO films and emerging as a potential candidate for ITO films.

**9:30 AM F1.3**
ELECTRICAL CONDUCTION MECHANISM OF HIGHLY TRANSPARENT AND CONDUCTIVE ZnO THIN FILMS. Tadatsugu Minami, Shingo Suzuki, Toshihiro Miyata, Kanazawa Institute of Technology, Optoelectronic Device System R&D Center, Ishikawa, JAPAN.

In this paper, we describe the underlying theory along with experiments concerning the electrical conductivity of transparent conducting ZnO films with a carrier concentration on the order of $10^{19}$-$10^{21}$ $cm^{-3}$. Undoped and impurity-doped ZnO thin films were prepared on glass and sapphire substrates by magnetron sputtering. The resistivity, carrier concentration and Hall mobility were measured over the temperature range of 77-300K using the van der Pauw method. The resistivity in ZnO films with an electron concentration of $10^{20}$-$10^{21}$ $cm^{-3}$ was found to be relatively independent of temperature in this temperature range. The mobility measured in undoped ZnO films increased as the electron concentration was increased in the range of $10^{19}$-$10^{20}$ $cm^{-3}$; however, mobility measured in impurity-doped ZnO films decreased as the electron concentration was increased in the range of $10^{20}$-$10^{21}$ $cm^{-3}$. From the results of the theoretical analysis and the experimental examination of electron mobility, we found that the mobility measured in ZnO films with an electron concentration of $10^{19}$-$10^{20}$ $cm^{-3}$ was mainly dominated by grain boundary scattering. In contrast, the mobility measured in ZnO films with an electron concentration of $10^{20}$-$10^{21}$ $cm^{-3}$ was mainly dominated by ionized impurity scattering with both degeneracy and nonparabolicity of the conduction band taken into account. Concerning the nonparabolicity, the conduction band effective mass as a function of carrier concentration was theoretically analyzed and experimentally determined. As a result, the experimentally determined mobility as a function of electron concentration in the range of $10^{19}$ to $10^{21}$ $cm^{-3}$ could be quantitatively referenced to a theoretically calculated mobility that is dominated by not only grain boundary scattering but also ionized impurity scattering using the Brooks-Herring-Dingle theory with both degeneracy and nonparabolicity of the conduction band taken into account.

**9:45 AM F1.4**
ELECTRICAL AND OPTICAL PROPERTIES OF $In_2O_3$ZnO AMORPHOUS TRANSPARENT CONDUCTIVE FILMS. Y Shigesato, N. Ito, P.K. Song, Aoyama Gakuin University, Tokyo, JAPAN; A. Kaijo, K. Inoue, Idemitsu Kosan Co., Ltd., Tokyo, JAPAN.

Amorphous transparent conductive films including amorphous ITO films have attract much attention because of the much higher wet etching rate and very flat surfaces. However, crystallinity of sputter deposited ITO films are reported to depend heavily on total gas pressure during deposition and fully amorphous films could be deposited only at rather high total gas pressure of 3-5 Pa with high reproducibility, even when the substrate temperature (Ts) was around RT[1,2]. K. Inoue reported that $In_2O_3$-ZnO (In/In+Zn=25-90 at%) films with entirely amorphous structure could be obtained under the wide range of deposition conditions such as total gas pressure or substrate temperature up to 300°. As such amorphous $In_2O_3$-ZnO films were also confirmed to show low resistivity of about 4∼5x$10^{-4}$ Ωcm, they are expected to be as new materials as transparent electrode especially for TFT-LCDs or organic ELDs.
In this study, a valence electron control on amorphous $In_2O_3$-ZnO films was investigated in order to increase carrier density (n). The

films were deposited by dc magnetron sputtering using the oxide ceramic $In_2O_3$-Zn) target (89.3wt% $In_2O_3$ and 10.7wt% ZnO, Idemitsu Co. Ltd). All the films were deposited without substrates heating, where valence electron control were tried by the following two methods, (a) introducing $CF_4$ gas for F-doping, or (b) introducing $H_2$ gas for the generation of oxygen vacancies during the deposition. In the case of (a) n decreased significantly by introducing $CF_4$ gas, whereas in the case of (b) n increased from 3.08x10 to 7.65x10 $cm^{-3}$ by introducing $H_2$ gas. The lowest resistivity of 3.39 x $10^{-4}$ Ωcm was obtained for $H_2$ gas flow ratio of 10% without substrate heating.
1. P.K. Song, Y. Shigesato, et al.. Jpn J. Appl. Phys. Vol. 38 (1999) 2921.
2. P.K. Song, Y. Shigesato, et al., Jpn J. Appl. Phys. Vol. 37 (4) (1998) 1870.
3. K. Inoue, Kinouzairyou, Vol. 19, No. 9 (1999) 39.

**10:00 AM F1.5**
HIGHLY (0001)-TEXTURED ZINC OXIDE THIN FILMS GROWN IN A MID-FREQUENCY MAGNETRON SPUTTERING PROCESS. X. Jiang, Fraunhofer-Institut für Schicht- und Oberflächentechnik, Braunschweig, GERMANY; C.L. Jia, Institut für Festkörper-forschung, Forschungszentrum Jülich GmbH, Jülich, GERMANY; B. Szyszka, Fraunhofer-Institut für Schicht- und Oberflächentechnik, Braunschweig, GERMANY.

A highly (0001)-textured ZnO:Al film structure generated directly on the nucleation sites via a mid-frequency magnetron sputtering is identified in high-resolution transmission electron microscopic images. In contrast with previously established mechanism of film texture formation in a vapor deposition process, our results show ZnO:Al texture neither dependent on the substrate structure, nor on the grain evolution selection during film growth. A surface energy-controlled step-flow mechanism was proposed, which is related with the process modes. In the metallic sputtering mode the films show a perfect columnar structure starting already at the film-substrate interface. In the oxide mode, however, a random film structure is revealed. The dependence of film properties on the film structure will be demonstrated and discussed. This work enhances the understanding of the texture formation and the potential applications.

**10:30 AM *F1.6**
LOOKING FOR NEW TCOS: A COMBINATORIAL APPROACH TO TCO SYNTHESIS AND CHARACTERIZATION. J.D. Perkins, X. Li, D.L. Young, P.A. Parilla, T.J. Coutts, D.S. Ginley, National Renewable Energy Laboratory, Golden, CO; C. Duncan, Colorado School of Mines, Golden, CO.

Tin-oxide and indium-tin-oxide are both good transparent conducting oxides (TCOs) and have, for many years, been the standard materials for a wide range of TCO applications. However, in recent years the desire for improved TCOs, particularly an increased carrier mobility, has driven the search for new TCOs to materials which are compositionally ever more complex. For example, the spinel $Cd_2SnO_4$ has demonstrated a higher mobility than $SnO_2$. CdO also has higher mobility than $SnO_2$, but, due to its lower band gap energy, is yellower in color. Extending this idea of blending simple single metal TCOs in search of new TCOs opens up the possibility of ternary, quatenary and possibly even more complex combinations of materials based on a multidimensional compositional phase space with CdO, $SnO_2$, $In_2O_3$, $Ga_2O_3$ and ZnO vertices. Additionally, the recent development of viable p-type TCOs and hence the possibility of active electronics composed of p and n-type TCO junctions should enable a new class of electronics. To optimize these complex materials systems, we are developing combinatorial tools and techniques for the deposition and analysis of TCO thin film libraries. A new three gun sputtering system has been built with one two inch gun and two one inch guns for co-sputtering of combinatorial libraries with intentional composition gradients from ceramic metal oxides targets. Our initial experiments are focussed on the simpler system $Zn_{1-x}Al_xO$. The ternary system combining CdO, $SnO_2$and ZnO will also be explored. Using an existing CVD deposition system, combinatorial libraries for the binary $CdO/SnO_2$ system have been grown. In this latter approach, the different decomposition temperatures for the dimethylcadmium and tetramethyltin precursors produce a varying Cd/Sn ratio along the gas flow axis. Libraries have been grown where the Cd/Sn ratio varies continuously from 3 to 1. These various combinatorial libraries will be characterized by UV-VIS-NIR transmission/reflection to look at the band gap, FTIR based IR-reflectivity to look at the plasma edge, which is related to the carrier density and Raman scattering to look for crystal structure changes. All of these optical spectroscopy measurements are inherently non-contact diagnostics and hence ideally suited to combinatorial analysis when coupled with automated sample translation. Selected samples will also be characterized with x-ray diffraction and electrical transport measurements.

**11:00 AM F1.7**
DEVELOPMENT OF PLASMA-ENHANCED CHEMICAL VAPOR DEPOSITION FOR THE SYNTHESIS OF TRANSPARENT CONDUCTING OXIDES. Joshua J. Robbins, Mailasu Bai, Yeng-Jung Huang, Tyrone Vincent, and Colin A. Wolden, Colorado School of Mines, Department of Chemical Engineering, Golden, CO.

Transparent conducting oxides (TCOs) are deposited almost exclusively by either physical vapor deposition (sputtering, pulsed laser deposition) or thermal chemical vapor deposition. Plasma-enhanced chemical vapor deposition (PECVD) offers unique advantages over both of these processes, particularly for the synthesis of novel alloys and doped structures. We have investigated the potential of PECVD for synthesis of tin oxide from mixtures of $SnCl_4$ and $O_2$. These films were deposited on glass substrates at temperatures between 150 and 350°C. The films' structural, optical, and electrical properties were examined as a function of plasma power, substrate temperature, pressure, and gas composition. In this talk we discuss the relationships between plasma operating conditions and film properties. Experiments revealed that plasma power and substrate temperature were strongly coupled. We demonstrate that PECVD may be used to deposit highly transparent, ultrasmooth TCO films at significant rates. In addition, excellent electrical properties may be obtained at relatively low substrate temperatures. Through proper choice of processing conditions films with a resistivity of 2 × $10^{-3}$ Ω-cm have been achieved at temperatures ≤ 250°C. Optical emission spectroscopy (OES) was employed to investigate the plasma composition. A rudimentary growth mechanism for the process was developed using both OES and film property measurements. We will also report briefly on current work that involves extending to PECVD to the zinc oxide material system and strategies for both doping and alloy formation.

**11:15 AM F1.8**
ELECTRICAL, OPTICAL, AND STRUCTURAL PROPERTIES OF FLUORINE-DOPED CdO. T.M. Barnes[a], Xiaonan Li, Clay DeHart, Helio Moutinho, Sally Asher, Yanfa Yan, Timothy A. Gessert, [a]Dept. of Chemical Engineering, Colorado School of Mines, Golden, CO; National Renewable Energy Laboratory, Golden, CO.

Cadmium oxide is a transparent conducting oxide (TCO) with very high mobility. The electrical properties of CdO could make significant contributions to understanding the function of Cd-containing ternary TCO materials. We have investigated the effects of fluorine doping and deposition temperature on CdO grown by metal organic chemical vapor deposition (MOCVD) using $(CH_3)_2Cd$, $O_2$, and $CBrF_3$. Fluorine doping increases the carrier concentration of the films by approximately one order of magnitude, but only slightly decreases the mobility. It also makes the electrical properties of the films less sensitive to changes in deposition temperature. At 300°C, F doping increases the conductivity by 130%, but only decreases the mobility by 30%. The films are not saturated with F at our maximum doping level, so the carrier concentration still could improve with increased doping. CdO has a very low effective mass, so increasing the carrier concentration by F-doping yields a significant Burstein-Moss shift. The optical bandgap is largest for the doped film grown at °C because it has the highest carrier concentration. The optical bandgap of the films decreases with increasing temperature because the carrier concentration decreases, but it is always higher in the doped films than in the undoped films. The optical bandgaps of these films vary from 2.4 eV to 2.85 eV. Doping with F allows CdO films to grow continuously at temperatures above 350°C, which is nearly impossible for the undoped films. Higher deposition temperatures improve the crystal structure of the film, thus the films have a much higher mobility than the films grown at lower temperatures. The highest Hall mobility of 262 $cm^2$/V-s with carrier concentration of $3.8*10^{19}$ / $cm^3$ was achieved at a deposition temperature of 450°C.

**11:30 AM F1.9**
TRANSPARENT CONDUCTIVE TIN DOPED INDIUM OXIDE THIN FILMS WITH SILVER ADDITIVE. A. Hultåker, J. Lu, E. Olsson, G.A. Niklasson, and C.G. Granqvist, Dept of Materials Science, Uppsala University, SWEDEN.

Tin doped indium oxide (ITO) is one of the most commonly used transparent conducting materials. Desired properties are high luminous transmittance combined with a resistivity of about $10^{-3}$ - $10^{-4}$ Ωcm. It is essential to study the microstructure of ITO because of its strong correlation to the optical and electrical properties. Adding a small amount of silver to ITO can boost the conductivity. However, the silver may also cause enhanced absorptance. Reactive dc magnetron sputtering was used to prepare thin films of intermixed layers of ITO and silver. The silver content in the different samples was 0 to 9 mole percent (mol%). The optical properties were modelled by Maxwell-Garnett effective medium theory, which allowed an estimation of the amount of silver present as particles in the films. A silver content of 1% yielded an increase in the luminous transmittance for films that had been post-treated at 100 and 200°C. Higher silver contents made the transmittance decrease as a consequence of

absorption in the silver particles. Films made with up to 6 mol% of silver additive showed enhanced electrical conductivity, by as much as a factor of two, after post-treatment at 200 or 300°C. The microstructure of the layers was studied by transmission electron microscopy. Pure ITO films have smooth columnar crystals growing from the substrate and upwards. The silver appears to distort the ITO crystals as well as the grain boundaries. We believe that the decrease in conductivity upon addition of 9 mol% of silver is caused by increased scattering due to these effects.

**11:45 AM F1.10**
ROLE OF SURFACES AND INTERFACES FOR THE ELECTRONIC PROPERTIES OF CONDUCTING OXIDES.
Andreas Klein, Darmstadt University of Technology, Darmstadt, GERMANY.

Transparent conductive oxides (TCOs) as indium oxide ($In_2O_3$), tin dioxide ($SnO_2$) and zinc oxide (ZnO) are widely used in electronic and optoelectronic circuits. They are generally considered as degenerate semiconductors doped intrinsically by oxygen vacancies and by intentionally added dopants. It is accepted that the Fermi level lies in the conduction band for high doping levels. For some applications a high workfunction is required in addition to high conductivity and it is desired to tune both properties independently. However, to increase the workfunction, the distance between the Fermi energy and the vacuum level must increase, which can be obtained either by electronic dipoles or by band bending. Photoelectron spectroscopy data of in-situ prepared samples clearly show that TCOs show surface band bendings of the order of 1eV. It is further shown that the band alignment at heterointerfaces between TCOs and other materials, which are crucial for many devices, are also affected by such band bending. The origin of the band bending, which seems to be general to all TCOs, its dependence on TCO thin film and surface processing conditions and its implication on electronic properties are discussed.

SESSION F2: TRANSPARENT CONDUCTING OXIDES II
Chairs: David C. Paine and Timothy J. Coutts
Tuesday Afternoon, April 17, 2001
Salon 3/4 (Marriott)

**1:30 PM *F2.1**
FLUORINE DOPING ON INDIUM OXIDE FILMS DEPOSITED BY RF MAGNETRON SPUTTERING.
Y. Shigesato, N. Shin, P.K. Song, College of Science and Engineering, Aoyama Gakuin University, Tokyo, JAPAN; M. Kamei, National Inst for Research in Inorganic Materials, Ibaraki, JAPAN; I. Yasui, Inst of Industrial Science, University of Tokyo, Tokyo, JAPAN.

Sn-doped $In_2O_3$ (ITO) is an n-type, highly degenerate, wid-gap semiconductor. Free carrier density (n) up to $10^{21}$ $cm^{-3}$ is known to be dominated by the following two different kinds of donor sites: (1) substitutional four-valent $Sn^{4+}$ ions ([Sn*]) at three-valent $In^{3+}$ sites and (2) oxygen vacancies ([V**]). As new candidates, other cation doping elements, such as Te, Ti, Zr, Hf, Nb, Ta, W and Ge were studied on $In_2O_3$, where n increased up to $10^{20}$ $cm^{-3}$ for Te, Zr and HF, however none of them were more effectve than Sn. On the other hand, anion doping of fluorine (F) could be worth trying because the ion radius of F- (1.36 A) is close to that of $O^{2-}$ (1.40 A) and substitutional replacement of F-with $O^{2-}$ is expected.
In this study fluorine-doped $In_2O_3$ films were deposited by rf magnetron sputtering using an $In_2O_3$ target at substrate temperatures from RT to 300° under Ar gas pressure of 1.0 Pa. The fluorine odping was carried out by the following two methods, (1) placing $InF_3$ pellets on the erosion area of the $In_2O_3$ target, and (2) introducing $CF_4$ gas into the sputtering chamber[1]. In both cases a systematic increase in carrier density (n) was observed, i.e. in case (1): n increased from $3.1x10^{19}$ to $2.9x10^{19}$ to $1.1x10^{20}$ $cm^{-3}$ by placing optimum number of $InF_3$ pellets and in case (2): n increased from $3.1x10^{19}$ to $1.1x10^{20}$ $cm^{-3}$ by introducing $CF_4$ gas $CF_4/(Ar+CF_4)$ flow ratio of 4%. The fluorine content of the fluorine-doped films was estimated by electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS), where the inclusion of fluorine was observed to increase by about 30% (F/In atomic%) in both cases.
1. Y. Shigesato, N. Shin, M. Kamei, P.K. Song and I. Yasui, Jpn. J. Appl. Phys. Vol. 39 Part 1, No.11(2000).

**2:00 PM *F2.2**
DETERMINATION OF BAND ALIGNMENTS OF TRANSPARENT CONDUCTIVE OXIDES.
Hideo Hosono, Iwao Yagi, Hiroshi Yanagi, Kazushige Ueda, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN; Hiroshi Mizoguchi, Hiromichi Ohta, Masahiro Hirano, Hosono Transparent ElectroActive Materials, ERATO, JST, Kawasaki, JAPAN.

Invention of transparent p-type conducive oxide is opening a pavement of application of transparent conductive oxides (TCO) to invisible circuits as exemplified by realization of uv-emitting diode entirely composed of TCOs, p-$SrCu_2O_2$ and n-ZnO. It is indispensable for facilitation of material exploration and devise design to make band alignments covering both n- and p-type semiconductors. Although such an alignment was established in III-V semiconductors, no effort on TCOs has been reported so far. We determined a band alignment of TCOs by measuring ultraviolet photoemission spectra (UPS), inverse photoemission spectra (IPES), and optical absorption spectra. The TCOs examined are (n-type) $CaTiO_3$, $TiO_2$, ZnO, CdO, $InGaZnO_4$, $In_2O_3$, $MgIn_2O_4$, $AgInO_2$, $SnO_2$, (p-type) NiO, $Cu_2O$, $CuGaO_2$, $SrCu_2O_2$, LaCuOS. The fresh surfaces were obtained by cleaning with a diamond file in a HV chamber($10^{-10}$ torr) and data collecting within 30min for UPS or 60min for IPES after then were used for consideration. The work function was determined from the cutoff energy of photoelectrons. The following conclusions were obtained from consideration about the band alignment determined here. (1) The top of valence band in the $Cu^+$-based p-type TCOs is shifted upward by $\sim$ 2eV. This observation substantiates that the valence band top is composed of covalent Cu-O bonds. (2) The valence band top of n-type TCOs is located at 7 $\sim$ 8eV from the vacuum level except CdO and $AgInO_2$.

**2:30 PM F2.3**
PREDOMINANT SCATTERING MECHANISM IN TRANSPARENT CONDUCTIVE OXIDE FILMS.
M. Chen, J. Chen, Y.H. Yu, X. Wang, Ion Beam Laboratory, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai, CHINA; Z.L. Pei, C. Sun, L.S. Wen, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, CHINA.

The widely worldwide market of flat panel display is promising a stimulation of the present research of TCO films. Fabrication of as low as possible resistivity with retaining high transparency in visible region is the aim of many works having been done on TCO films. Most works have been concentrated on three systems: $In_2O_3$:Sn ITO, $SnO_2$:F and ZnO:Al{ZAO}. Of all the TCO films present, ITO and $SnO_2$:F have the best electrical properties. Many works about the preparation, characteristic, electrical and optical properties of TCO films have been reported in various literatures, and a large number of experimental data of electrical and optical properties have been given out, but till up to now, the films with the resistivity of lower than $1.0\times 10^{-4}\Omega$·cmare difficult to be fabricated. The question is whether we can obtain the TCO films with a resistivity of lower than $1.0\times 10^{-4}\Omega$·cmare order in the same time having a high visible transmittance, and what is main scattering mechanism of transparent conductive oxide films. This paper is concerned to illustrate the fundamental physical limit on the electrical properties of TCO system based on the analysis of various main scattering mechanisms, summarize reported experimental electrical data and give a specific graph on the electrical properties of TCO films. The basic intention in the paper is try to give a lower limit to the attainable resistivity regardless of scattering mechanism, the presence or absence of which depends on the precise details of the preparation procedure. The results indicate that the contributions of acoustical scattering and boundary potential scattering on the conductivity of TCO films are proved to be insignificant. It is also suggested that the ionized impurity scattering is the intrinsic limit on the conductivity of TCO films only based on the two corrections: one is the effective mass correction and the other is the relationship correction between carrier concentration and ionized impurity centers. In spite of the two corrections, two experiential expressions were obtained to illustrate the upper limit of mobility and the lower limit of resistivity of TCO films regardless of the sophisticated consideration of effective mass correction and carrier concentration correction.

**2:45 PM F2.4**
INTERNAL STRESS OF ITO, GZO AND IZO FILMS DEPOSITED BY DC AND RF MAGNETRON SPUTTERING.
T. Sasabayashi, P.K. Song, Y. Shigesato, Aoyama Gakuin University, Tokyo, JAPAN.

Mechanical properties such as internal stress or adhesion of transparent conductive oxide (TCO) films are quite important to guarantee the patterning accuracy and the durability for various kinds of commercial applications. In this study, representative TCO films, such as tin doped indium oxide (ITO), gallium doped zinc oxide (GZO) and indium zinc oxide (IZO) films, were deposited on glass substrate at room temperature (lower than 50°) by dc and rf magentron sputtering using oxide targets under various total pressure ($P_{tot}$) from 0.3 to 3.0 $Pa._{1,2}$. The internal stress ($\sigma_{1nt}$) of these TCO films was estimated by cantilever method using 30, 50 and 100 $\mu$m thick micro-sheet glass substrates in relation to the film thickness (50-810nm) and the various deposition conditions including various magnetic field shapes and strength of the sputtering cathode. 200 nm thick ITO films deposited with the 250G standard balanced magnet at $P_{tot}$ lower than 0.7 Pa were polycrystalline and showed high

compressive stress, while the amorphous ITO films deposited at 1.5~3.0 Pa showed a very slight tensile stress. On the contrary, the all IZO films with various thicknesses (50-750 nm) deposited at $P_{tot}$ of 0.3~3.0 Pa showed entirely amorphous structure, where the compressive stress of IZO films was extremely lower than that of ITO films. The relationships between the microstructure and the internal stress of various TCO films will be discussed in detail.

1. P.K. Song, Y. Shigesato, et al., Jpn. J. Appl. Phys. Vol. 38, (1999) 2921.
2. P.K. Song, Y. Shigesato, et al., Jpn. J. Appl. Phys. Vol. 37 (4) (1998) 1870.

**3:00 PM F2.5**
CRYSTALLIZATION OF AMORPHOUS INDIUM TIN OXIDE.
Hyo-Young Yeom, Courtney Lanier, E. Chason, and David C. Paine, Brown University, Division of Engineering, Providence, RI.

In the slightly sub-stoiciometric crystalline form of indium oxide, n-type carriers donated by doubly charged oxygen vacancies (and substitutional four valent Sn) creates a degenerate semiconductor that is widely used for transparent electrode applications. Deposition of indium (tin) oxide onto cool (room T) substrates by sputter deposition results in an initially amorphous structure that crystallizes at remarkably low temperatures (<150°C) relative to the indium oxide melting point (1910°C). Technological trends requiring lower resistance material deposited onto heat intolerant polymer substrates has created increased interest in the electrical/optical performance of amorphous indium tin oxide and the kinetics of its crystallization.We have studied the crystallization of amorphous indium oxide deposited by DC magnetron sputtering using ceramic targets with 0, 2.5, and 9.8 wt% $SnO_2$ reactively sputtered under low oxygen (0 vol %), optimum oxygen (with respect to conductivity), and high (10 vol %) oxygen conditions. Transport measurements obtained during isothermal annealing (110<T<250°C) simultaneously with wafer curvature were used to determine the effect of changes in the amorphous and crystalline structure on carrier density and mobility. For example, annealing of crystallized indium oxide in oxygen leads to the oxidation of excess vacancies, a surprising decrease in resistivity, and an increase in molar volume. Curvature/transport measurements combined with Kroger-Vink diagrams have been used to provide insight into oxygen vacancy configurations and mechanisms for maximizing carrier density in low temperature deposited indium oxide. Finally, in situ TEM was used to directly observe the crystallization of ITO and to (1) establish a model that relates volume fraction crystalline material to changes in resistivity, and (2) the temperature and compositional (Sn) dependence of the nucleation of crystalline islands and reaction rates at the amorphous/crystalline interface. The technological implications and opportunities presented by the a/c-transformation in this system will be discussed.

**3:30 PM *F2.6**
A THEORETICAL PROPOSAL FOR P-TYPE DOPING OF ZnO.
Y. Yan, S.B. Zhang, National Renewable Energy Lab., Golden, CO; S.J. Pennycook, and S.T. Pantelide, Oak Ridge National Lab, Oak Ridge, TN.

Zinc oxide has long been recognized as a possible material for short-wavelength light-emitting diodes and laser diodes. To realize this device application, an important issue is to fabricate both p-type and n-type ZnO with low resistance. While ZnO can be doped n-type to very low resistance using group III elements, Si and F, it has not been possible to dope p-type with adequate hole concentrations and mobilities. The reasons for the problem are not fully understood. In this work, we report first-principles calculations in terms of which we account in detail for recent puzzling reports of high concentgrations and low mobility or vice versa obtained with codoping by N and Ga. Furthermore, the calculations allow us to identify an alternative process that promises both high hole concentration and high mobility.

**4:00 PM F2.7**
TRANSPARENT P-TYPE CONDUCTING LaCuOS LAYERED OXYSULFIDE.
Kazushige Ueda, Shin-ichiro Inoue, Sakyo Hirose, Hideo Hosono, Tokyo Institute of Technology, Materials and Structures Laboratory, Yokohama, JAPAN; Hiroshi Kawazoe, HOYA Corporation, R&D Center, Akishima, JAPAN.

Transparent p-type conducting oxides, $CuMO_2$ (M=Al, Ga) and $SrCu_2O_2$, have been found recently on the basis of the materials design that the modulation of the valence band by chemical bonds between oxygen $2p^6$ and Cu $3d^{10}$ orbitals increases the mobility of positive holes in transparent oxides. The essence of this materials design is not limited to oxide materials, because it is applicable to chalcogenide materials if oxygen might be regarded as a chalcogen element. A LaCuOS layered oxysulfide was selected as a candidate for a transparent p-type conducting material. The crystal structure of LaCuOS is composed of LaO and CuS layers alternately stacked along the c-axis. This layered structure is considered to provide transparent p-type conducting character to the material: the LaO layers widen the energy gap of LaCuOS and the CuS layers act as conduction paths. $La_{1-x}Sr_xCuOS$ (x=0, 0.05) thin films were prepared by radio-frequency sputtering. The films were found to have high optical transmission (≥70 %) in the visible-infrared region and an energy gap of about 3.1 eV. The dc electrical conductivities of x=0 and 0.05 thin films at room temperature were $1.2\times10^{-2}$ and $2.6\times10^{-1}$ $Scm^{-1}$, respectively. The Seebeck coefficients of these samples were positive, indicating that p-type electrical conduction is dominant in these materials. A sharp photoluminescence peak, probably originating from an exciton, was observed at the optical absorption edge. The present study demonstrates that LaCuOS is a promising transparent p-type semiconductor for optoelectronic applications. In addition, the materials design, based on the chemical modulation of the valence band, was successfully extended to oxysulfide systems.

**4:15 PM F2.8**
GROWTH OF P-TYPE POTASSIUM-DOPED $SrCu_2O_2$ TRANSPARENT THIN FILMS.
Renaud Stauber, University of Colorado, Physics Department, Boulder, CO; John Perkins, Phil Parilla, David Ginley, National Renewable Energy Lab, Golden, CO.

Recent progress has been made in the development of p-type transparent conducting oxides. $SrCu_2O_2$ is of considerable interest as it is able to be processed at temperatures below 350°C and can be doped with potassium. We report here on the deposition of thin films of strontium copper oxide ($SrCu_2O_2$) with and without K doping and their electro-optical characterization. $SrCu_2O_2$ films were prepared by pulsed laser deposition (PLD). Preliminary Hall measurements of a 2% K-doped film indicate p-type conductivity with a carrier density of $3*10^{16}$ $cm^{-3}$ and a mobility of .6 $cm^2/V$-s. The optical bandgap of this film was estimated to be 3.3eV from optical transmission measurements and remained highly transparent out to 2500nm. The variation of carrier density and other electro-optical parameters with K-doping and PLD parameters will be described. The effects of deposition properties on crystal structure and phase formation have also been studied. PLD targets were synthesized with 0, 2%, 4% and 6% (molar %) potassium substituted for strontium. Phase pure targets were made by annealing pressed powders at 950°C in flowing $N_2$ for 25 hours. The targets sintered below 925°C had various Sr-Cu-oxide impurity phases, and those annealed at 1050°C began to melt. Crystallinity and stoichiometry were assessed by x-ray diffraction, and x-ray photoelectron spectroscopy.

**4:30 PM F2.9**
DEEP-UV TRANSPARENT CONDUCTIVE $\beta$-$Ga_2O_3$ Film.
Masahiro Orita, Hiromichi Ohta, Masahiro Hirano, Hosono project of Transparent ElectroActive Materials, JST, Kasasaki, JAPAN; Hideo Hosono, Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

A need for deep-ultraviolet (UV) transparent conductive oxide (TCO) films has recently emerged for use half tone layers of phase shift masks for photolithography and as transparent electrodes for UV optoelectronic devices. Two deep-UV transparent TCO materials have been reported so far: polycrystalline $ZnGa_2O_4$ and single-crystal $\beta$-$Ga_2O_3$. Both materials exhibit high electrical conductivity in bulk form, but no transparent conductive thin films have been obtained from them, despite efforts. $\beta$-$Ga_2O_3$ belongs to space group C2/m, in which $Ga^{3+}$ ions occupy both octahedral and tetrahedral sites. A tetravalent tin ion was chosen as the dopant because the ionic radius of $Sn^{4+}$ is close to $Ga^{3+}$, and $Sn^{4+}$ ions prefer 6-fold coordination, they tend to substitute the $Ga^{3+}$ octahedral sites. We set a low oxygen partial pressure of ambient atmosphere and an elevated substrate temperature, which could enlarge chemical potential of oxygen in the lattice and could result in formation of oxygen defects and $Sn^{4+}$ solution into the lattice by releasing oxygen gas into the atmosphere. Thin films of $\beta$-$Ga_2O_3$ with an energy bandgap of 4.9 eV were successfully prepared on silica glass substrates by a pulsed-laser deposition method. N-type conductivity up to 1 $Scm^{-1}$ was obtained by deposition under low $O_2$ partial pressure ($10^{-5}$ Pa) at substrate temperatures above 800°C. The resulting internal transmittance at the wavelength (248nm) of the KrF excimer laser exceeded 50% for the 100nm-thick film, making this the most ultraviolet-transparent conductive oxide thin film to date.

**4:45 PM F2.10**
COMBINED BULK AND THIN-FILM COMPARATIVE STUDY OF THE NOVEL TRANSPARENT CONDUCTING OXIDE SOLUTION $Cd_{1-x}In_{2-2x}Sn_xO_4$.
Daniel R. Kammler and Thomas O. Mason, Northwestern University, Dept. MS&E, Evanston, IL; David L. Young and Timothy J. Coutts, National Renewable Energy Laboratory, Golden, CO.

Future Transparent Conducting Oxides (TCOs) for use in applications such as photovoltaics and flat panel displays will require increased mobilities. Reports of high mobilities in oxides along the binaries of

the CdO-$In_2O_3$-$SnO_2$ system suggest the interior may contain novel high-mobility TCO phases and or solutions. A combination bulk/thin film investigation has been used to deal with the increased complexity of this multi-cation system. Bulk phase relations at 1175 C show single phase spinel $Cd_{1-x}In_{2-2x}Sn_xO_4$ for $0 \leq x \leq 0.75$ and a bi-phasic region for $0.75 < x < 1.0$ consisting of orthorhombic $Cd_2SnO_4$ and the terminal spinel composition. Bulk 4-point DC conductivity is relatively constant at 2500 S/cm between x = 0 and 0.4 and increases rapidly until 0.6 where it remains near 3500 S/cm until the solution terminates for specimens reduced in 4 % $H_2$, 96% $N_2$ at 400 C for 6 hrs. Single phase spinel targets of compositions corresponding to x = 0.15, 0.45 and 0.70 along $Cd_{1-x}In_{2-2x}Sn_xO_4$ were produced for the film study. Films were deposited via rf-magnetron sputtering in oxygen and annealed at 660°C for 60 min in Ar or Ar/CdS. Conductivities (Ar/CdS anneal) increased from 2000-2600 S/cm for x=0.15 to 4000-4300 S/cm for x=0.45. Mobility increased from 42-45 $cm^2$/V-s (x = 0.15) to 49-51 $cm^2$/V-s (x=0.45). Carrier densities varied from 2.9-3.9 x $10^{20}$ 1/$cm^3$ (x = 0.15) to 5.0 - 5.3 x $10^{20}$ 1/$cm^3$ (x= 0.45). Preliminary results from the x = 0.70 films indicate conductivities near 4000 S/cm, mobilities near 60 $cm^2$/V-s and carrier densities near 4 x $10^{20}$ 1/$cm^3$. Optical gaps (Ar/CdS anneal) varied from 3.4-3.6 eV for x = 0.15 films to 3.6-3.8 eV for the x=0.45 films. Specialized equipment at NREL is being used to study the variation in effective mass and scattering time in $Cd_{1-x}In_{2-2x}Sn_xO_4$. Initial measurements show non-parabolic bands and an increase in scattering time with x for the most highly doped films from 6.7 to 10.3 x $10^{-15}$ s as x increases from 0.15 to 0.70. This may explain the increase in mobility with x.

SESSION F3: POSTER SESSION
TRANSPORT AND MICROSTRUCTURAL PHENOMENA IN OXIDE ELECTRONICS
Chairs: Marilyn E. Hawley and Stephen K. Streiffer
Tuesday Evening, April 17, 2001
8:00 PM
Salon 1-7 (Marriott)

**F3.1**
ELECTRICAL CHARACTERISTICS OF THE Pt/SBT/$TiO_2$/Si MFIS STRUCTURES WITH THICKNESS VARIATION OF THE SBT FILM. Ji-Woong Kim, Kwang-Yong Lee, Jae-Hoon Choi, Tae-Sung Oh, Hong Ik Univ, Dept of Metallurgical Engineering and Materials Science, Seoul, KOREA.

Pt/$SrBi_{2.4}Ta_2O_9$/$TiO_2$/Si structures were prepared with variation of the $SrBi_{2.4}Ta_2O_9$ (SBT) film thickness for metal ferroelectric insulator semiconductor field effect transistor (MFIS-FET) applications. After depositing $TiO_2$ film of 10 nm thickness by reactive sputtering on Si(100) substrate as a buffer layer, SBT thin film of 150-400 nm thickness was prepared onto it by metalorganic decomposition (MOD) process. Regardless of the SBT film thickness, the Pt/SBT/$TiO_2$/Si structures exhibited clockwise directional hysteresis, indicating well-defined ferroelectric switching behavior of the SBT film. While the memory window of the Pt/SBT/$TiO_2$/Si MFIS structures increased with increasing the SBT film thickness, the maximum capacitance of the Pt/SBT/$TiO_2$/Si MFIS structures increased with decreasing the SBT film thickness. The Pt/SBT(400 nm)/$TiO_2$(10 nm)/Si structure exhibited a memory window of 1.6 V at ±5 V.

**F3.2**
SPIN GLASS-LIKE BEHAVIUOR IN THE COLOSSAL MAGNETORESISTIVE $La_{0.6}M_{0.1}Ca_{0.3}MnO_3$ (M = Ho (MAGNETIC) AND Y(NON-MAGNETIC)) COMPOUNDS. V. Ravindranath and M.S. Ramachandra Rao, Materials Science Research Centre and Department of Physics Indian Institute of Technology Madras, Chennai, INDIA.

Electron correlation effects are of great interest in manganese perovskites such as $La_{1-x}M_xMnO_3$ (M=Ca, Sr, Ba etc.) since they exhibit colossal magnetoresistance (CMR) close to the ferromagnetic transition temperature ($T_C$). In the present study $La_{0.6}M_{0.1}Ca_{0.3}MnO_3$ (M = Ho and Y) compounds were prepared to study and understand the effect of doping a magnetic ion (Ho) in comparison with a nonmagnetic ion (Y) both having almost the same ionic radius ($Y_{i.r}$=1.018Å, $Ho_{i.r}$=1.015Å). Magnetisation measurements show a large deviation in the FC and ZFC measurements for the Y compound at low temperatures indicating a spin-glass like behaviour. However, in the case of Ho (0.1) - doped compound the deviation is very marginal. We have also observed shifts in the peak temperature with variation in frequency using ac-susceptibility technique confirming spin glass like behaviour. The magnetic frustration in these systems is due to the decrease in the overall ferromagnetic exchange interactions by either the decrease in the $Mn^{4+}$ concentration or the mobile charge carrier density [1,2]. In this case the effects due to both the above mentioned factors are the same and so the observed differences in the behaviour of the Y and Ho compounds could be attributed to the magnetic nature of the Ho ion. The relatively smaller spin glass-like behaviour in the Ho-compounds could be explained in terms of an increase in the ferromagnetic exchange interactions due coupling of the Ho-magnetic moment with that of the Mn-moment. Charge carrier density measurements are underway. References: [1]. N. Gayathri et al. Phys. Rev. B. 56 (1997) 1345. [2]. M. Rubinstein et al. J. Appl. Phys. 81 (1997) 4974.

**F3.3**
STRUCTURAL AND ELECTRICAL PROPERTIES OF COLOSSAL MAGNETORESISTIVE LSMO THIN FILMS PREPARED BY KrF LASER ABLATION METHOD. Fumiaki Mitsugi, Tomoaki Ikegami, Kenji Ebihara, Kumamoto Univ, Dept of Electrical and Computer Engineering and Graduate School of Science and Technology, Kumamoto, JAPAN; Jagdish Narayan, North Carolina State Univ, Dept of MS&E, NC; Alexander M. Grishin, Royal Institute of Technology, Dept of Condensed Matter Physics, Stockholm, SWEDEN.

We fabricated $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) films on MgO, $SrTiO_3$ (STO) and $LaAlO_3$ (LAO) (100) single crystal substrates by KrF excimer laser deposition method. The lattice mismatch of the LSMO film with MgO, STO and LAO substrates defined as $(a_{LSMO}\text{-}a_{sub})/a_{sub}$ are -7.8%, -0.5% and 2.4%, respectively. The X-ray diffraction patterns of the LSMO films on the above substrates exhibited the c-axis oriented LSMO (00n) peaks. In case of the LSMO/LAO films, the divided (00n) peaks were observed. This result suggests that the stress of LSMO/LAO film is attributed to the formation of two different layers. The LSMO/LAO thin film (100nm) had relatively high resistivity and low magnetoresistance. On the other hand, the LSMO/MgO and LSMO/STO thin films did not have dislocations and showed low resistivity (<20 mΩ·cm). The LSMO (200nm)/MgO thin film had MR ratio of 15% at room temperature. The optimum thickness of the LSMO films on MgO, STO and LAO was found to be 200-300 nm, 150-240 nm and 450-1000 nm, respectively. The LSMO films having the resistivity peak temperature in the range from 340 K to 350 K exhibited excellent colossal magnetoresistive characteristics at room temperature.

**F3.4**
MANGANITE THIN FILMS GROWN USING PLD: STUDY OF STRAIN AND ANNEALING EFFECTS. M.S. Ramachandra Rao, V. Ravindranath, Materials Science Research Centre and Department of Physics, Indian Institute of Technology Madras, Chennai, INDIA; Y. Lu, J. Klein, R. Gross, II. Physikalisches Institut, Universitat zu Köln, Köln, GERMANY.

Mixed valency of Mn ($Mn^{3+}/Mn^{4+}$) is required to realize the metallic behaviour as well as ferromagnetism in colossal magnetoresistive (CMR) manganites. Double exchange (DE) mechanism in conjunction with the effect of lattice distortion in manganites [1] is responsible for the occurrence of the CMR property. Recently, we have shown [2] that substitution of magnetic Ho- ions compared to non-magnetic Y-ion at the La - site in $La_{0.7-x}R_xCa_{0.3}MnO_3$ (R = Ho (magnetic) and Y) causes a large decrease in resistivity. Both Ho and Y have almost identical ionic radii ( $Ho_{i.r.}$ = 1.018° and $Y_{i.r.}$ = 1.015°) and hence the internal (lattice) strain leading to changes in tolerance factor is the same in both the case. Pulsed laser deposition (PLD) technique was used to grow thin films of 0.05 compositions of Y and Ho doped compounds on polished $SrTiO_3$ (STO) substrates. Interestingly, the slight lattice mismatch between STO and LCMO has further decreased the $T_C$ (strain due to mismatch) down to 125 K (160 K on the bulk compounds). In addition to the decrease in $T_C$, the changes in resistivity are the same as that observed in the case of polycrystalline samples, i.e., Ho doped films have less resistivity compared to Y-doped LCMO films. Reflection high energy electron density (RHEED) technique was used to monitor the in-situ growth of the film and low angle XRD revealed excellent crystallinity of the films. Atomic force microscopy (AFM) studies showed excellent surface morphology. Resistivity measurements (rho vs T) were done at 0 and 8T and the conduction process, in these doubly strained films, in the insulating regime have been studied using standard models. Studies on the effect of ex-situ annealing on $T_C$ and microstructure are underway. References: 1. H.Y. Hwang et al. Phys. Rev. Lett. 75 (1995) 914. 2. V. Ravindranath et al. Submitted to Phys. Rev. B. 3. J. Klein et al. J. Magn. Magn. Mater. 211 (2000) 9.

**F3.5**
DIELECTRIC PROPERTIES AND LEAKAGE CURRENT CHARACTERISTICS OF $Al_2O_3$ THIN FILMS WITH THICKNESS VARIATION. Jae-Hoon Choi, Ji-Woong Kim, Tae-Sung Oh, Hong Ik Univ, Dept of Metallurgical Engineering and Materials Science, Seoul, KOREA.

$Al_2O_3$ thin films of 10-300 nm thickness were deposited on

$Pt/Ti/SiO_2/Si$ and Si substrates by reactive sputtering at room temperature. Effects of the $O_2$ content in the sputtering gas on the dielectric properties and leakage current characteristics of the $Al_2O_3$ films were investigated with emphasis on the thickness dependence of the dielectric properties. The $Al_2O_3$ films of 10-300 nm thickness were amorphous regardless of the $O_2$ content ranging from 25% to 75% in the sputtering gas. Maximum dielectric constant was obtained for the $Al_2O_3$ films deposited with the sputtering gas of the 50% $O_2$ content. With reduction of the film thickness from 300 nm to 10 nm, dielectric constant decreased from 9.04 to 3.71 and tangent loss increased from 0.0035 to 0.0594, respectively. When the $O_2$ content in the sputtering gas was within 50% to 75%, the $Al_2O_3$ films exhibited no shift of the flatband voltage in C-V curves. The $Al_2O_3$ films of 100 nm thickness exhibited leakage current density lower than $10^{-6}$ A/cm$^2$ at 650 kV/cm.

**F3.6**
VARIABLE RANGE HOPPING CONDUCTANCE IN MAGNETRON SPUTTERED AMORPHOUS SILICON SUBOXIDES. J.J.van Hapert, E.E. van Faassen, A.M. Vredenberg, F.H.P.M. Habraken, Debye Institute, Interface Physics, Utrecht University, THE NETHERLANDS.

The tunable resistivity of amorphous $SiO_x$ makes it a promising material for applications in printing devices. However, the structural and electronic properties of these materials are not well understood. We investigate structural and electronic properties of magnetron sputtered a-$SiO_x$. Thin layers (500 nm) of silicon sub-oxides with different oxygen content ($0< x< 2$) were deposited at low temperatures (<80°C). ESR measurements indicate that defect densities are high (>$10^{20}$ cm$^{-3}$). The temperature dependence of the electrical conductivity indicates that these defects determine the conduction through the variable range hopping (VRH) mechanism. VRH conduction is observed even up to room temperature. This provides a good opportunity to investigate the VRH process.
In this presentation we focus on the electric field dependence of the VRH conduction. At low electric field strengths a 'normal' log $\sigma \sim T^{-1/4}$ behavior is observed. However, as a consequence of the VRH model, a temperature independent non-Ohmic conduction mechanism is expected at high electric field strengths. Measurements indeed show this uncommon behavior. The transition temperature between $T^{-1/4}$ and T-independent conduction is uniquely defined by the localization parameter of the defects involved in the conduction. We will show both measurements and analyses and the effect of composition (oxygen concentration) on the localization parameter.

**F3.7**
DIELECTRIC PROPERTIES ANALYSIS IN PARAELECTRIC $ZrTiO_4$ THIN FILMS DEPOSITED BY DC MAGNETRON SPUTTERING. Kyunghae Kim, Junsin Yi, School of Electrical and Computer Engineering, Sungkyunkwan, KOREA; Byungwoo Park, School of Materials Science and Engineering, Seoul National, KOREA.

Single-phase paraelectric $ZrTiO_4$ thin film deposited by direct-current magnetron reactive sputtering method. We used platinum as the top electrode and very high phosphorou-doped Si(100) as the bottom electrode. X-ray diffraction patterns for the films deposited at room temperature exhibited amorphous characteristics with only the Si peaks. Above 400°C, polycrystalline $ZrTiO_4$ peaks appeared in the films with (111), (020), (011) and (202) planes. After annealing in an oxygen atmosphere for 2 hours at 800°C, the films showed an improved polycrystalline characteristics. The dielectric losses ($\tan\delta$) stayed less than $10^{-2}$ for a measurement frequency of 100kHz. As the deposition temperature increased, the dielectric losses ($\tan\delta$) decreased from 0.038 to 0.017, while the dielectric constants (*epsilon*) were in the range of 35. Post anneal treament reduced $\tan\delta$ down to 0.005. The measured dielectric constants of the thin films dropped as the frequency increase. We designed an equivalent circuit and compared the measured data with values of the equivalent circuit model. This paper carried out optimization of $ZrTiO_4$ film deposition to achieve high quality $\epsilon_r$ and $\tan\delta$ characteristics.

**F3.8**
STRUCTURAL, OPTICAL, AND ELECTRON TRANSPORT QUALITIES OF ZINC STANNATE THIN FILMS. David L. Young, Timothy J. Coutts, National Renewable Energy Laboratory, Golden, CO; Don L. Williamson, Colorado School of Mines, Dept. of Physics, Golden, CO.

Zinc stannate (ZTO = $Zn_2SnO_4$), an exceptionally transparent, conducting oxide (TCO), is an attractive material for TCO applications because of its low cost and low toxicity. Despite its unfavorable mobilities and carrier concentrations, ZTO has recently been utilized in world-record CdTe/CdS thin-film solar cells. This paper reports on measuring fundamental crystallographic, optical, and electron transport quantities of ZTO thin-films. Single-phase, spinel ZTO thin films were grown by rf magnetron sputtering onto glass substrates. Uniaxially oriented films with resistivities of $10^{-2}$ - $10^{-3}$ Ω·cm, mobilities of 16 - 26 cm$^2$/V-s, and n-type carrier concentrations in the low $10^{19}$ cm$^{-3}$ were reproducible. X-ray diffraction peak intensity studies identified the films to be in the inverse spinel configuration. Mössbauer studies using $^{119}$Sn identified two octahedral Sn sites, each with a unique quadrupole splitting, but with a common isomer shift consistent with Sn 4. A fundamental, direct bandgap of 3.35 eV was extrapolated from transmittance and reflectance data. A pronounced Burstein-Moss shift moved the optical bandgap to as high as 3.89 eV in the highest carrier-concentration film of 3.3 x $10^{19}$ cm$^{-3}$. *The method of four coefficients* (conductivity, Hall, Seebeck and Nernst) was applied to the films to reveal the density-of-states effective mass, relaxation time, mobility, Fermi energy level, and a scattering parameter. The density-of-states effective-mass value was found to increase with carrier concentration from 0.16 to 0.26 $m_e$ as the Fermi energy increased from 0.2 to 0.9 eV above the conduction-band minimum. First-order nonparabolic conduction-band theory was applied to extrapolate a bottom-of-the-band effective mass of 0.15 $m_e$. Calculated scattering parameters and temperature-dependent transport measurements correlated well with ionized impurity scattering with screening by free electrons for highly degenerate films. Possible phonon-like and grain-boundary scattering mechanisms were determined to be negligible for ZTO films. Relaxation times were on the order of 1-3 x $10^{-15}$ s.

**F3.9**
$InSbO_4$: A NEW N-TYPE TRANSPARENT CONDUCTIVE OXIDE DEPOSITED BY RF MAGNETRON SPUTTERING. Y. Shimada, P.K. Song, Y. Shigeasto, Aoyama Gakuin University, Setagaya-ku, Tokyo, JAPAN; T. Hattori, M. Ishida, K. Saegusa, Sumitomo Chemical Co., Ltd., Tsukuba Research Laboratory, Ibaraki, JAPAN.

Considerable efforts have been focused on depositing thin films of transparent conducting oxides (TCOs) with significantly reduced resistivity in order to accommodate the increasing technological demand for larger area flat panel displays with higher image quality. In recent years, multicomponent oxides composed of binary and/or ternary compounds have attracted much attention as new materials for the TCO films. In this study Indium antimonate ($InSbO_4$), the rutile structure in which $In^{3+}$ and $Sb^{5+}$ ions occupy the random cation positions, has been investigated as a new n-type TCO candidate because computer calculations implied the lower electron effective mass of $InSbO_4$ than that of ITO. $InSbO_4$ thin films were deposited on $SiO_2$-coated Si wafer ($SiO_2/Si$) or fused glass substrates at 400°C by rf magnetron sputtering. As the sputter targets a sintered ceramic disk of $InSbO_4$ was used, where several antimony metallic pellets were placed on the erosion area in order to control the atomic ratio (Sb/In) precisely in the films. Ar was used for the sputtering gas and $O_2$ was also introduced to adjust the stoichiometry of the films. The all films were annealed at 900°C in the atmosphere before the electrical and structural characterizations. The film deposited using the target with 4 antimony pellets and oxygen flow ratio of 0% showed a minimum resistivity of $6.43\times10^{-3}\Omega\cdot$cm, where the carrier concentration and mobility were $1.84\times10^{20}$cm$^{-3}$ and 5.29 cm$^2\cdot$V$^{-1}\cdot$s$^{-1}$ at room temperature, respectively. Hall effect measurement on the films with various Sb/In showed that carrier density increased systematically with the increase in Sb/In, implying that the excess $Sb^{5+}$ was substituted for $In^{3+}$ resulting in the carrier generations. Possibility of Sn, Mo or W dopings into $InSbO_4$ will be also discussed in detail.

**F3.10**
MOBILITY IN TIN OXIDE THIN POLYCRYSTALLINE FILMS: GRAIN BOUNDARY EFFECT AND SCATTERING IN THE GRAIN BULK. A.S. Gilmore, A. Al-Kaoud, V.I. Kaydanov, and T.R. Ohno, Colorado School of Mines, Dept of Physics, Golden, CO.

Basic electronic properties relevant to the carrier mobility were studied in $SnO_2$:F thin films prepared by atmospheric pressure chemical vapor deposition. Electrical resistivity, Hall and Seebeck effects, plasma and collision frequencies were measured (the last two by using multiangle spectral ellipsometry) and analyzed for films with carrier concentrations from $1.8\text{x}10^{20}$ to $5.6\text{x}10^{20}$ cm$^{-3}$. Scanning over the sample area of resistivity (four-point probe method) and Seebeck coefficient (thermoprobe) monitored uniformity of electronic properties in plane. Ellipsometry was used to check uniformity over the film thickness. Films with a thickness above 400 nm demonstrated high spatial uniformity and were used for further studies. The effective mass was determined from combined Hall and plasma frequency measurements and was found to be independent of carrier concentration, which indicates a parabolic band spectrum. Its value was very close to the literature data. In films with carrier concentration $\geq3\text{x}10^{20}$ cm$^{-3}$ the Hall mobility was very close to the optical mobility calculated based on collision frequency and effective mass values. This indicates a very small contribution of grain boundaries to the total resistivity of films. Thus the measured

mobility is close to the electron mobility in the grain bulk. The scattering parameter value derived from thermopower measurements along with the temperature independent mobility indicated that electron scattering by impurity ions screened by free carriers is the dominating scattering mechanism. Theoretical estimates of mobility are very close to the highest measured mobility values ($\geq$30 $cm^2/Vs$) if the spatial dispersion of the dielectric constant is taken into account. Comparison of differently processed films showed that compensation of donor dopant with uncontrolled acceptor centers significantly impacted the mobility.

**F3.11**
INFRARED TRANSPARENT CONDUCTING $CuAlO_x$, $CFeO_x$, $CuCrO_x$ and $CuYO_x$ DEPOSITED BY REACTIVE MAGNETRON SPUTTERING. Linda F. Johnson and Mark B. Moran, Naval Air Warfare Center Weapons Division, Research Department, China Lake, CA.

Amorphous films of $CuAlO_x$, $CuFeO_x$, $CuYO_x$ and $CuCrO_x$ were deposited by reactive magnetron co-sputtering from high-purity-metal targets. Films with improved microstructure and optoelectronic properties were obtained using an asymmetric-bipolar-pulsed-dc-power supply. A 2200-Å-thick-$CuFeO_x$ coating has a resistivity of 0.00024ohm-cm, a sheet resistance of 11ohms/sq and transmission greater than 95% in the mid-wave infrared. Similar to the copper-based high-temperature superconductors, the presence of Cu-O bonds is critical. Fourier transform infrared (FTIR) and electron spectroscopy for chemical analysis (ESCA) were used to understand the relationship between the optoelectronic properties and the molecular structure of the films. For example, FTIR absorption bands at 1470 and 1395 $cm^{-1}$ are present only in $CuAlO_x$ films that exhibit enhanced electrical conductivity. When these bands are absent, the $CuAlO_x$ films have high values of resistivity. Similar phonon bands at 1080 and 990 $cm^{-1}$ are observed in $CuFeO_x$. It is important to note that the frequencies of these doublets scale inversely with the square root of the atomic masses of Fe and Al. These bands may involve cumulated Cu=O=Al=O=Cu or Cu=O=Fe=O=Cu double bonds along the c-axis of the respective delafossite compounds. Cumulated Cu=O=Al=O=Cu bonds would require $p_z$ orbitals on O to overlap with $p_z$ orbitals on Al and $d_z{}^2$ orbitals on Cu atoms. Higher-order bonding could result from an oxygen deficiency on the Al or Fe atom in the respective delafossite, $CuAlO_x$ or $CuFeO_x$. The delafossite structure mimics the structure of high-temperature-superconducting-copper oxides on an atomic scale. Recently, Berkeley researchers used scanning tunneling microscopy to show that short-range order is very important in determining the properties of high-temperature superconductors. The doublet absorption bands may be associated with the phonon-assisted-electrical conduction and Cooper-pair phenomena that are used to explain superconductivity. Hall-effect measurements also show that our $CuAlO_x$ films are p-type so phonons probably are involved in the enhanced conductivity.

**F3.12**
Abstract Withdrawn.

**F3.13**
PHOTOLUMINESCENT PROPERTIES OF ZINC OXIDE THIN FILMS GROWN BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION. W.I. Park, S.-J. An, Gyu-Chul Yi, and Hyun M. Jang, Pohang University of Science and Technology (POSTECH), Dept of MS&E, Pohang, KOREA (SOUTH).

There has been much attention to the growth and optical characterizations of ZnO for short-wavelength photonic device applications. For the ZnO film growth, numerous deposition techniques including sputtering, pulsed laser deposition, molecular beam epitaxy (MBE), and metal-organic chemical vapor deposition (MOCVD) have been employed. Although strong stimulated emission was observed from high quality ZnO epilayers grown by MBE, stimulated emission from MOCVD-grown ZnO has not yet been reported. In this presentation, we report on the strong stimulated emission and photoluminescent properties of ZnO films grown by MOCVD. The ZnO layers were grown on $Al_2O_3$(0001) and $SiO_2$/Si substrates using a low pressure MOCVD system. As-grown ZnO films were highly transparent and specular. For the optical characterization of the films, photoluminescence (PL) spectra of the ZnO films were measured at 15-300 K. Several near bandedge emission peaks including exciton transitions were observed from the PL spectra measured at 15 K. Based on the temperature-dependent PL spectra, the origin of the PL peaks will be discussed. Meanwhile PL spectra at room temperature exhibited a broad peak at 3.23-3.24 eV when the 325 nm line with a low excitation intensity of 1 $W/cm^2$ was illuminated on the films. For the high excitation intensity of 0.5 $MW/cm^2$, however, a very sharp and strong stimulated emission peak was observed at 3.173 eV. The full width at half maximum of the emission peak was as narrow as 6-7 meV.

**F3.14**
BIPOLAR ELECTRICAL CONDUCTIVE TRANSPARENT OXIDE, $CuInO_2$. Hiroshi Yanagi, Kazushige Ueda, Hideo Hosono, Tokyo Institute of Technology, Materials and Structures Laboratory, Yokohama, JAPAN.

A transparent oxide semiconductor with delafossite structure, $CuInO_2$, was found to exhibit both p- and n-type conduction by doping of an appropriate impurity and tuning of film-deposition conditions. This is a first transparent conductive oxide (TCO) with delafossite structure exhibiting bipolarity in electrical conduction. We selected $CuInO_2$ as a candidate on the basis of our chemical design for finding p- and n-type TCOs. $CuInO_2$ delafossite was prepared by cation exchange reaction using $NaInO_2$ and CuCl. Substitution for $In^{3+}$ with $Ca^{2+}$ or $Sn^{4+}$ was carried out for acceptor- or donor-doping, respectively. In the preparation of doped $CuInO_2$, Sn 5% doped or Ca 7% doped $NaInO_2$ was used as precursor. Thin films of Sn- or Ca-doped $CuInO_2$ were prepared on sapphire substrates by pulsed laser deposition. The films were deposited at 723 K in $P_{O_2}$ = 1.5 Pa atmosphere for the Sn-doped films or 1.0 Pa for the Ca-doped films. The conductivity of Sn-doped films was very sensitive to partial $O_2$ pressure during deposition. The conductive Sn-doped films were successfully prepared in the narrow range of $P_{O_2}$ from 1.4 to 1.6 Pa. The conductivity of films deposited in $P_{O_2} > 2.0$ Pa became fairly low ($<10^{-6}$ S/cm). The crystal quality of the films deposited in $P_{O_2} < 1.3$ Pa was considerably poor as a consequence of decomposition. The Seebeck coefficient of the Sn-doped film at room temperature was -50 $\mu$V/K. This negative sign demonstrated n-type conduction in the Sn-doped film. The conductivity at 300 K was 0.004 S/cm. On the other hand, the Seebeck coefficient of the Ca-doped film was 480 $\mu$V/K indicating p-type conductivity. The conductivity of Ca-doped film was 0.003 S/cm at 300 K. The optical band gap of each film was estimated to be $\sim$3.9 eV. The fabrication of p-n homojunction utilizing this material is next issue in our on-going research.

**F3.15**
TRANSPARENT CONDUCTING INDIUM-TIN-OXIDE THIN FILM WITH EXTREMELY FLATTED SURFACE. Hiromichi Ohta, Masahiro Orita, Masahiro Hirano, Hosono Transparent ElectroActive Materials, ERATO, JST, JAPAN; Hideo Hosono, Tokyo Institute of Technology, JAPAN.

Transparent conducting indium-tin-oxide thin films with extremely flatted surface were grown heteroepitaxially on (111) surface of YSZ by a pulsed-laser deposition (PLD) technique. An increase in substrate temperature up to 900°C, use of YSZ(111) instead of YSZ(100) as a substrate is a key factor to improve the surface roughness. The crystallinity of the ITO thin film was very high; full width at half maximum of out-of-plane rocking curve of X-ray diffraction was 54 seconds. Atomically flat terraces and steps corresponding to (222) plane spacing were clearly observed by an atomic force microscopy (AFM). The overall surface roughness of the ITO film evaluated by grazing incidence X-ray reflection was less than 0.2nm, which agreed with the value probed locally by an atomic force microscopy (AFM).

**F3.16**
GROWTH AND CHARACTERIZATION OF ZnO FILMS ON SAPPHRIE SUBSTRATE BY THE HELICON WAVE PLASMA ASSISTED EVAPORATION PROCESS. Kyoung-Bo Kim, Tae-Hee Park, Seon-Hyo Kim, Pohang University of Science and Technology, Dept of MS&E, Pohang, SOUTH KOREA.

Since Boswell proposed that helicon waves were efficient in producing plasma even at low pressures of about $10^{-4}$ Torr, concerns about the helicon wave plasma (HWP) source have been voiced because of its potential application to thin film fabrication. HWP has been adopted in various material processes such as etching and film deposition. Those thin film processes show advantages of high ionic flux ($> 10^{13}$ $cm^{-3}$) and independent control of impinging ion energy. However, there are few reports concerning the use of HWP to produce the reactive oxygen species required for the epitaxial growth of oxide semiconductors. We believe that the HWP source could be utilized in growing epitaxial oxide thin films at a high growth rate by virtue of the high flux and low kinetic energy of reactive oxygen species. In particular, ZnO (Eg $\approx$ 3.3 eV at room temperature) analogous to GaN has some interesting properties such as large bond strength and extreme stability of excitons (binding energy $\approx$ 60 meV), and may be useful for efficient UV laser applications at practical device temperatures. In this study, a HWP source (Ar $O_2$) was used to synthesize a ZnO thin film on sapphire (0001) substrate with evaporated Zn vapor. The grounded grids were installed at the exit of the plasma source to eliminate oxygen ions and selectively extract reactive neutrals. When the grounded grids were installed, charged species were significantly reduced. The crystallinity and luminescent properties for ZnO films deposited with grounded grids were much better than those for ZnO films without grounded grids. This result indicates that ion bombardment is severely reduced by the installation

of grounded grids. Hence, we expect the HWP assisted evaporation process to become one of the more important techniques for growing ZnO thin films.

**F3.17**
MOCVD ZINC OXIDE FILMS FOR DEVICE APPLICATIONS. Jeffrey E. Nause, Cermet, Atlanta, GA; Gary Tompa, Structured Materials Industries, Inc., Piscataway, NJ; Dave Look, Wright State University, Semiconductor Research Center, Dayton, OH.

Recent literature citations indicate an increase in the research and development of zinc oxide for a range of applications. Some of this research has been directed at substrate or buffer layer development for nitride devices. Increasingly, zinc oxide researchers intend to use zinc oxide as short wavelength light emitters in the blue-to-ultraviolet portion of the spectrum. To that end, the focus of the research has been in two main areas; the growth of high quality, zinc oxide substrates, and the identification of a suitable p-type dopant for zinc oxide. This work describes a program to grow zinc oxide films with a range of compositions on zinc oxide substrates. The films were grown with MOCVD. The deposition approach will be outlined. The electrical, structural, and optical properties of the films will be presented.

**F3.18**
DOPING EFFECTS ON CdO THIN FILMS. Xiaonan Li, Timothy Gessert, Timothy Coutts, National Renewable Energy Laboratory, Golden, CO.

Among the various studies of transparent conducting oxide (TCO) thin films, few have been devoted to cadmium oxide (CdO). One reason is that the bandgap of CdO is around 2.4 eV, which is smaller than bandgap of other TCO materials such as $In_2O_3$:$SnO_2$ (3.4 eV) and $SnO_2$ (3.6 eV). However, previous studies indicate that Cd-containing compounds may have the advantage of enabling high mobilitya prerequisite for high conductivity TCO materials with minimal free-carrier absorbance. This paper will report on the properties of undoped CdO films, doped with the group IV element Sn, and the group VII element F. The CdO films were made by low-pressure chemical vapor deposition with dimethylcadmium and oxygen. Film properties were studied using Hall probe measurements, spectrophotometry, X-ray diffraction, and secondary ion mass spectrometry. We observed that the undoped CdO film could achieve a carrier concentration of $10^{21}$ /cm$^3$, apparently by controlling the intrinsic defect. However, the electron mobility of these films is very low. Our CdO:F films have achieved electron mobilities ~260 cm$^2$/V-s, but demonstrate low carrier concentration due to the low solubility of F in CdO. CdO films doped with both Sn and F demonstrate carrier concentration of $10^{21}$ /cm$^3$ and reasonable electron mobility of around 20 cm$^2$/V-s. Due to the small effective-electron mass of CdO, a large Burstein-Moss (BM) shift is observed for films with high carrier concentration. The shift has enabled the fundamental absorption edges of undoped CdO films to reach 3.37 eV, and the films doped with both Sn and F to reach 3.27 eV. We believe the high mobility and the high transmittance enabled by the larger BM shift may allow CdO films to be considered for use in several optoelectronic devices.

**F3.19**
MICROSTRUCTURE AND RESISTIVITY OF ITO THIN FILMS PREPARED BY ION BEAM SPUTTER DEPOSITION. Younggun Han, Seon-Ju Kwon, Jun-Sik Cho, Seok-Keun Koh, Thin Film Research Center, Korea Institute of Science and Technology, KOREA; Donghwan Kim, Department of Materials Science and Engineering, Korea University, KOREA.

Tin-doped indium oxide (ITO) films were deposited on glass substrates by ion beam sputtering. The effect of seed layer on the crystallinity and microstructure of the deposited films was investigated using x-ray diffraction and scanning electron microscopy. The seed layers were prepared by ion beam sputtering where sputter gases were pure Ar gas, and mixture gas of Ar and oxygen, respectively. The microstructure of the grown films is significantly dependent on the seed layers. Domain and grain structure are observed in the films with the seed layers deposited by ion beam sputtering using pure Ar and mixture gas, respectively. The electrical properties of the deposited ITO films were examined by four point probe and Hall measurement, and explained in terms of the change of the microstructure and crystallinity.

**F3.20**
OPTICAL AND STRUCTURAL PROPERTIES OF ZINC OXIDE THIN FILM DEPOSITED BY PULSED LASER DEPOSITION. Tamiko Ohshima, Raj Kumar Thareja, Yukihiko Yamagata, Tomoaki Ikegami, Kenji Ebihara, Kumamoto Univ, Graduate School of Science and Technology, and Dept of Electrical and Computer Engineering, JAPAN.

Zinc oxide (ZnO) is II-VI semiconductor with great potentials in acoustic, electronic, and optical applications, particularly in low voltage phosphorescent displays. Here we report on the optical and structural properties of ZnO thin films deposited by pulsed laser deposition technique. ZnO thin films were deposited on glass and silicon substrates using KrF laser (248nm). We have studied the influence of the deposition parameters, such as substrate temperature, oxygen pressure, and laser fluence on the properties of the grown films. Laser fluence on the target was in the range from 1 to 5J/cm$^2$. The pressure of the abmient oxygen gas for the growth of ZnO film was varied from 2 to 10mTorr, and the growth temperature from 350 to 700°C. Structural and optical properties of as grown thin films were investigated using X-ray diffraction (XRD), atomic force microscope (AFM), UV-visible transparency. The XRD pattern of the films showed that the diffraction peaks broadened as the oxygen pressure was reduced, indicating smaller grain size with lower oxygen pressure. The average diameter of nanocrystallites is estimated by using the broadening of the diffraction peaks in the Sherrer's formula. Size of nanocrystallites is found to be less than 15nm in the pressure range studied. The crystalline morphology of the films was studied using AFM. Films grown at lower oxygen pressures are smoother than those deposited at higher oxygen pressure. In order to prepare high quality ZnO thin films, a detailed spectroscopic investigation of the properties of the plume produced during film deposition was undertaken. An attempt is made to correlate the properties of the deposited film with that of plasma characteristics.

**F3.21**
CHARACTERIZATION OF ZINC OXIDE THIN FILMS DEPOSITED BY RF MAGNETRON SPUTTERING ON MYLAR SUBSTRATES. Elvira Fortunato, Patrícia Nunes, Daniel Costa, Donatello Brida, Andreia Machado, Isabel Ferreira, Rodrigo Martins, FCT-UNL, Caparica, PORTUGAL.

Highly transparent and conducting Al-doped zinc oxide (ZnO:Al) thin films have been prepared by the first time on polyester (Mylar type D, 100 micron thickness) substrate at room temperature by rf magnetron sputtering. The structural, optical and electrical properties of the deposited films have been studies. The samples are polycrystalline with a hexagonal wurtzite structure and a strong crystallographic c-axis orientation (002) perpendicular to the substrate surface. The ZnO:Al thin films with a 83% transmittance in the visible region and a resistivity as low as $3.6x10^{-2}$ Ohmcm have been obtained, as deposited and without deterioration of the substrate. The films were grown under different rf power and were characterised by: X-ray diffraction, HRSEM; HRTEM, Hall effect and optical transmittance. The obtained results are comparable to those ones obtained in glass substrates, opening a new field of low cost, light weight, small volume, flexible and unbreakable large area optoelectronics devices.

**F3.22**
THIN FILM GROWTH OF ZINC OXIDE BY VAPOR PHASE EPITAXY. Jim Ellis, Bill Seng, Peter Barnes, Auburn Univ, Dept of Physics, Auburn, AL.

Zinc Oxide (ZnO) is a potentially valuable semiconductor with photoconducting, piezoelectric, optoelectronic, and optical waveguide applications. A technique for the growth of ZnO epitaxial layers is necessary for improved device fabrication. Previously, attempts at ZnO epitaxial growth were constrained to sapphire substrates using sputtering as the preferred preparation technique. However, with the present availability of single crystal ZnO substrates the hope of high quality epitaxial layers exists. The authors will discuss several possibilities for growth precursors, and the resulting chemical reactions required for the formation of ZnO. This presentation discusses the growth of ZnO epitaxial layers by chemical vapor deposition without using metal-organic compounds. The thermodynamics and predicted growth rates for several reactions are presented as well as the preliminary growth results. The preliminary growths are characterized with the aid of Hall Effect measurements, providing information on resistivity, Hall mobility, and carrier concentration.

**F3.23**
STABILITY AND REACTIVITY OF THIN FILM METALLIZATIONS OF ZnO. William F. Seng and Peter A. Barnes, Auburn University Department of Physics, Auburn, AL.

Recently there has been interest in semiconductors able to operate at elevated temperatures. The production of ZnO electronic devices capable of operation at elevated temperatures requires an understanding of the chemical reactions at the metal-semiconductor interface. Applications requiring ohmic contacts or Schottky barriers require knowledge of the resulting phases which can be predicted from equilibrium thermodynamics. Significant changes in the transport characteristics and physical characteristics can occur due to the new

compounds formed. Reactions of the metal with the substrate ZnO not only consume substrate material, but also can additionally nullify the surface preparations of previous processing steps. Finding metals or metallic compounds which are thermodynamically stable and which do not react with the substrate over a desired temperature range of both device processing and operation can thus narrow the search for Schottky barriers or ohmic contacts. Results of thermodynamic calculations are presented as both Ellingham and Gibbs ternary diagrams to understand the temperature dependence of the formation and stability of interfacial films. Examples of metals reactive with ZnO (such as Mg) and stable metals (such as Ag) were deposited on ZnO and analyzed physically and electrically via AES/XPS, RBS, XRD and I-V. Results are compared with the thermodynamic predictions. The limitations of the thermodynamic approach are also discussed.

***F3.24**
THE MECHANICAL RELIABILITY OF INDIUM TIN OXIDE COATED POLYMER SUBSTRATES FOR FLEXIBLE DISPLAYS AND TOUCHSCREEN. Darran R. Cairns, David C. Paine and Gregory P. Crawford, Brown University, Division of Engineering, Providence, RI.

Indium tin oxide (ITO) films deposited on polyester substrates are a key material in the development of two exciting technologies, touchscreens and flexible liquid crystal displays. New portable devices are being developed which place greater demands on the substrate than was the case for traditional glass based displays. The new generation CEplastic displays and touchscreens must be flexible and robust, have excellent optical properties, and be inexpensive! Polyester substrates are ideally suited to these applications.
In this paper we report on the mechanical and electrical reliability of ITO on a polyethylene terephthalate substrate (PET). We report on the gradual increase in resistance with uniaxial strain for a variety of ITO thicknesses ranging from 16 nm to 150 nm, the evolution of fragmentation of the ITO layer in bending and tension, damage mechanisms in indentation and impact and wear damage of ITO in touchscreens. We show that the mechanical behavior of the ITO film is dominated by the properties of the substrate and that the deformation of the substrate is mapped by the crack patterns in the ITO. This is most strongly evidenced in the simulated wear of a touchscreen where failure after >50000 pen strokes is primarily due to cracking of the ITO as a result of increased substrate deformation over time. In addition the mechanical reliability of the ITO layer is dependent on the film thickness. Cracking was observed in a 105 nm thick ITO film at a strain of 0.022 and for a 16.8 nm thick film at 0.003. The thickness and hence sheet resistance of the film effectively limits the maximum allowable deformation of the substrate and must be considered in the design of suitable display and touchscreen devices. In addition we report on the change in resistance with time-at-temperature and relate this to the shrinkage of the substrate.

SESSION F4: OXIDE BASED DEVICES I
Chairs: John D. Perkins and Dave H.A. Blank
Wednesday Morning, April 18, 2001
Salon 3/4 (Marriott)

**8:30 AM *F4.1**
TRANSPARENT P-N HETEROJUNCTION THIN FILM DIODES. M.K. Jayaraj, A. Draeseke, J. Tate, Department of Physics, J.F. Wager, Department of Electrical and Computer Engineering, Oregon State University, Corvallis, OR.

Transparent p-n heterojunctions on glass substrates were fabricated using p-type $CuY_{1-x}Ca_xO_2$ and n-type $Zn_{1-x}Al_xO$ films. The diode was fabricated on a glass substrate coated with indium-tin-oxide (ITO) with the following structure: glass/ITO/ $Zn_{1-x}Al_xO$/ $CuY_{1-x}Ca_xO_2$. The contact between the n- $Zn_{1-x}Al_xO$ and p- $CuY_{1-x}Ca_xO_2$ semiconducting oxides was found to be rectifying, and the ITO/ $Zn_{1-x}Al_xO$ contact was ohmic. The ratio of forward to reverse current was above 20 in the range -3 - 3 V. The turn-on voltage varied between 0.7 - 0.9V on different junctions. The diode structure had a total thickness of 0.85 $\mu$ and had an optical transmission of 40%-50% in the visible region.

**9:00 AM *F4.2**
IMPROVEMENT OF UV-LIGHT EMISSION FOR P-N HETEROJUNCTION LED COMPOSED OF p-$SrCu_2O_2$ AND n-ZnO. Hiromichi Ohta, Masahiro Orita, Masahiro Hirano, Hosono Transparent ElectroActive Materials, ERATO, JST, JAPAN; Hideo Hosono, Tokyo Institute of Technology, JAPAN.

In order to improve UV-light emission efficiency of p-n heterojunction LED composed of p-$SrCu_2O_2$ and n-ZnO [REF], $SrCu_2O_2$ layer was grown heteroepitaxially on ZnO layer at higher substrate temperature of 600°C by pulsed-laser deposition technique. As results of HR-XRD study, Crystal orientation relationship were as follows, $SrCu_2O_2$ (100) // ZnO (0001) // ITO (111) // YSZ (111) and $SrCu_2O_2$ (011) // ZnO ($11\bar{2}0$) // ITO ($1\bar{1}0$) // YSZ ($1\bar{1}0$). Cross sectional TEM image indicated that interface between $SrCu_2O_2$ and ZnO was very abrupt and $SrCu_2O_2$ was grown heteroepitaxially on ZnO with single domain. The turn-on voltage of fabricated LED device was 3 V, which was corresponding with intrinsic energy gap of ZnO or $SrCu_2O_2$. UV (wavelength=382 nm) emission was observed when forward bias voltage was applied more than 3 V. Threshold current of UV emission was 2mA, which was 1/5 of the diode reported previously (Ith = 10mA). The leakage current due to lattice defects was decreased due to improvement of crystallinity at interface between $SrCu_2O_2$ and ZnO. [REF] H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, Electronics Letters, 36, 984 (2000); H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura, and H. Hosono, Appl. Phys, Lett., 77, 475 (2000).

**9:30 AM F4.3**
COMPOSITION-SPREAD EPITAXIAL THIN FILMS OF ONE DIMENSIONAL CUPRATES AS GIGANTIC OPITCAL NONLINEAR OXIDES. T. Fukumura, M. Ohtani, M. Kawasaki, Dept of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, JAPAN; K. Yamamoto, T. Makino, Y. Segawa, Photodynamics Research Center, RIKEN, Sendai, JAPAN; H. Koinuma, Frontier Collaborative Research Center, and Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

Very recently, gigantic third-order nonlinear susceptibility [1] and ultra-fast all optical switching [2] have been discovered in one-dimensional Mott insulator, $Sr_2CuO_3$. For the device application of these phenomena, one has to grow epitaxial thin films with desired orientation. Moreover, the control of the optical energy gap leading to the tunability of working wavelength aiming at optical communications and further enhancement of the nonlinearity are desired. A promising approach to them is substituting Sr with the other alkaline earth elements such as Ba and Ca. Here we report on the fabrication and optical properties of $(AE)_2CuO_3$ ($AE$ = Ba, Ca, Sr) composition-spread films. The composition-spread films were epitaxially grown on $LaSrAlO_4$ (100) substrates by a combinatorial laser MBE system [3]. The crystallinity of the composition-spread films was analyzed by a concurrent XRD system, that was developed for high throughput analysis of combinatorial thin films [3]. The orientation of the films was controlled to be $a$-axis normal to the surface so that the Cu-O chain was aligned in-plane along one direction. The lattice constant changes monotonously with the composition. The polarized transmission spectroscopy revealed that the film had large anisotropic absorbance, where the absorbance for the $E$ // $b$ axis (parallel to Cu-O chain) configuration was much larger than the perpendicular configuration. The energy shift in the charge transfer absorption was observed as a function of averaged ion size of $AE$ site. [1] H. Kishida et al., Nature 405, 929 (2000). [2] T. Ogasawara et al., Phys. Rev. Lett. 85, 2204 (2000). [3] T. Fukumura et al., Appl. Phys. Lett. November 20 issue (2000), in press.

**9:45 AM F4.4**
COEXISTENCE OF METALLIC AND INSULATING PHASE IN EPITAXIAL $CaRuO_3$ THIN FILMS. Sangjin Hyun, Jonghoon Cho, Ahram Kim, Tesu Kim, and Kookrin Char, Seoul National University, Center for Strongly Correlated Materials Research & School of Physics, Seoul, KOREA.

We have investigated the local conductivity of epitaxial $CaRuO_3$ thin films grown on $LaAlO_3$ substrates by pulsed laser deposition using scanning microwave microscope (SMM). SMM, composed of a quarter wavelength coaxial resonator, can investigate the local properties of materials in the rf/microwave frequency region by measuring the shifts of resonant frequency and the change of quality factor through the interaction with the probe and the sample in the near-field regime. From resistance versus temperature measurement, we found that the $CaRuO_3$ thin films had very different behavior depending on the growth temperature. While the $CaRuO_3$ thin films grown at 700°C showed metallic behavior, the $CaRuO_3$ thin films grown at 800°C showed semiconducting behavior, probably due to Ru deficiency. After scanning the semiconducting $CaRuO_3$ thin films with SMM, it was revealed that there existed metallic islands of various sizes in the sea of insulating phase of the $CaRuO_3$ films. We will discuss this coexistence of metallic and insulating phases in the context of the metal-insulator transition in epitaxial $CaRuO_3$ thin films.

**10:15 AM F4.5**
EXPLORING THE SURFACE PASSIVATION OF OXIDES ON SILICON FOR PHOTOVOLTAIC CELLS BY PULSED LASER DEPOSITION. Lianne Doeswijk, Arjen Janssens, Dave Blank, Horst Rogalla, University of Twente, Dept. of Applied Physics, Low Temperature Division, Mesa, Enschede, NETHERLANDS.

In the effort of combining antireflective and passivating properties in one coating for the use on silicon solar cells, we are exploring the possibilities of introducing passivating qualities in oxide coatings with pulsed laser deposition. To unravel why coatings show surface passivation, effort is undertaken to determine the extent and content of the interface between the coating and silicon substrate. Stoichiometric oxides ($TiO_2$, $SrTiO_3$, $BaTiO_3$) show no passivating qualities. The interface characteristics at the interface with silicon have to be altered. The first approach is to change the background gas in which deposition takes place. By depositing in an oxygen deficient ambient oxygen vacancies are introduced, which account for the presence of positive oxide charge in the coating. The second approach was to change the interface species present by using different cleaning procedures for the silicon substrates and ablation of different oxide materials (SrO, $SrSiO_4$, $SrTiO_3$, $TiO_2$). We will make clear that the interface properties play the key-role in passivation of the silicon surface, for which we will also show the importance of the oxide content at the surface.

**10:30 AM *F4.6**
MATERIALS AND DEVICE DESIGN WITH ZnO-BASED DILUTED MAGNETIC SEMICONDUCTORS. Kazunori Sato, Hiroshi Katayama-Yoshida, The Institute of Scientific and Industrial Research, Osaka University, Osaka, JAPAN.

Recently, ZnO attracts much attention as an optoelectronic material because of its wide band gap energy of 3.3 eV and large exiton binding energy of 60 meV. Its cheapness, abundance and harmoniousness with our environment are also appealing. Besides, unipolarity that prevents us from fabricating *p*-type ZnO had been overcome by using the codoping method [1], and now ZnO becomes one of the most promising materials in oxide electronics. To investigate its functionality as a diluted magnetic semiconductors (DMS), we had studied the magnetism in ZnO doped with 3*d* transition metal atoms (TM) and showed that it was also a candidate for a new functional magnetic material [2]. In this paper, we develop our previous work and give detailed materials design with ZnO-based DMS based on *ab initio* calculations. The electronic structure of a TM-doped ZnO was calculated within the local density approximation by the Korringa-Kohn-Rostoker method combined with the coherent potential approximation (KKR-CPA). The KKR-CPA method is one of the best ways to simulate substitutionally disordered alloys. Total energies of $Zn_{1-x}TM^{\uparrow}_{x}O$ and $Zn_{1-x}TM^{\uparrow}_{x/2}TM^{\downarrow}_{x/2}O$, where up and down arrows mean the directions of respective atomic magnetic moments, were compared and appearance of the ferromagnetism was discussed. Effects of carrier doping to these systems were also investigated. It was found that their magnetic states were controllable by changing the carrier density. It was also suggested that doped ZnO-based DMS had higher Currie temperature than the III-V based DMS and they had potential to realize practical ferromagnetic semiconductors. Some new devices, such as spin-FET, photo induced ferromagnet and so on, will be proposed in this paper. [1] T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys. **38** (1999) L166. [2] K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. **39** (2000) L555.

**11:00 AM *F4.7**
HIGH CONDUCTIVITY LANTHANUM COPPER OXIDE THIN FILMS FOR OXIDE ELECTRONICS. J.A. Misewich and A.G. Schrott, IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY.

Although oxide materials offer a wide variety of interesting and useful properties, an efficient field effect switch remains elusive. We have been exploring room temperature field effect transistor (FET) structures using normal state cuprate oxide channel materials.[1] However, the electric field mobility in these devices has previously been limited to 0.1 $cm^2$/V-sec. In the carefully studied case of lanthanum copper oxide channels, our studies indicate that the mobility has been limited by grain boundaries in the films. Recently we have fabricated high conductivity thin films of lanthanum copper oxide on lanthanum aluminate substrates. These films offer greater than an order of magnitude increase in conductivity compared to films grown on strontium titanate films. Field effect mobilities of 1 $cm^2$/V-sec were measured in buried oxide FET devices made on lanthanum aluminate substrates. [1] J.A. Misewich and A.G. Schrott, Appl. Phys. Lett. 76, 3632 (2000).

**11:30 AM F4.8**
FLUORINE AS A DONOR DOPANT IN BARIUM-TITANATE PTCR CERAMICS. Darko Makovec, Nina Ule and Miha Drofenik, Department of Ceramics, Jozef Stefan Institute, Ljubljana, SLOVENIA.

Donor-doped $BaTiO_3$ ferroelectric ceramics may be prepared in a semiconducting state by exaggerated grain growth during sintering in air. Such semiconducting ceramics display a PTCR effect - an abrupt increase in the resistivity at the Curie temperature. To achieve this condition, cationic donors, e.g. 3-valent ions substituted for Ba, or 5-valent ions substituted for Ti, are normally used. For thermodynamic reasons, sintering in air will result in exaggerated grain growth and, as a consequence, semiconducting ceramics only with low concentrations of cationic donor dopant (below $\sim$0.3 mol.%). This limits the preparation of PTCR ceramics with a high concentration of free-charge carriers by sintering in air and consequently the production of PTC resistors with low room-temperature resistivity. Apart from the usual cationic donors, fluorine substituted for oxygen may be used as the anionic donor dopant. In fluorine-doped $BaTiO_3$ ceramics the microstructural development is different to that observed in the conventional cationic donor-doped material, suggesting that semiconducting ceramics with high donor concentrations could be prepared. In the present work, defect chemistry, microstructural development and the resulting electrical properties of fluorine-doped $BaTiO_3$ ceramics have been studied as a function of starting composition and processing conditions. The samples in the $BaTiO_3$ - $TiO_2$ - $BaF_2$ system have been prepared using conventional ceramic technology. The incorporation of the fluorine dopants into the $BaTiO_3$ structure was studied using X-ray powder diffractometry, microscopy techniques and electrical measurements.

**11:45 AM F4.9**
CHARACTERISTICS OF THE Pt/SBT/$Al_2O_3$/Si STRUCTURES FOR MFIS-FET APPLICATIONS. Ji-Woong Kim, Jae-Hoon Choi, Tae-Sung Oh, Hong Ik Univ, Dept of Metallurgical Engineering and Materials Science, Seoul, KOREA.

Pt/$SrBi_{2.4}Ta_2O_9$/$Al_2O_3$/Si structures were prepared for metal ferroelectric insulator semiconductor field effect transistor (MFIS-FET) applications. After depositing $Al_2O_3$ film of 5-50 nm thickness by reactive sputtering on Si(100) substrate as a buffer layer, $SrBi_{2.4}Ta_2O_9$ (SBT) thin film of 400 nm thickness was prepared onto it by metalorganic decomposition (MOD) process. With annealing at 800°C for 1 hour in oxygen ambient, the 400 nm-thick SBT film exhibited $2P_r$ of 10.4 C/$cm^2$ and $E_c$ of 29.4 kV/cm at ±5V. C-V characteristics of the Pt/SBT/$Al_2O_3$/Si structures exhibited hysteresis loops due to the ferroelectric switching behavior of the SBT film. When the $Al_2O_3$ buffer layer was thicker than 10 nm, memory window and maximum capacitance of the Pt/SBT/$Al_2O_3$/Si structure increased with decreasing the thickness of the $Al_2O_3$ buffer layer, and the Pt/SBT(400 nm)/ $Al_2O_3$(10 nm)/Si structure exhibited a memory window of 1.8 V at 5 V.

SESSION F5: OXIDE BASED DEVICES II
Chairs: Jeremy Levy and Marilyn E. Hawley
Wednesday Afternoon, April 18, 2001
Salon 3/4 (Marriott)

**1:30 PM *F5.1**
GROWTH AND CHARACTERIZATION OF SELF-ASSEMBLED PALLADIUM OXIDE NANOSTRUCURES. Babu R. Chalamala, Robert H. Reuss, Motorola, Inc., Semiconductor Products Sector, Digital DNA Laboratory, Tempe, AZ; Yi Wei, Motorola Labs, Tempe, AZ; Sanjeev Aggarwal, R. Ramesh, University of Maryland, College Park, MD.

Currently, there is great interest in forming nanoscale structures through thermo-dynamically driven self assembly processes. For nanoelectronics, self-assembled processes hold the promise of enabling the creation of complex, next-generation device architectures that rely on the intrinsic ability of the system to organize itself into ordered patterns. This is in contrast to the artificially ordered schemes, such as that are currently used in integrated circuits. Many inorganic systems also display microstructural evolution that resembles self-assembled processes, for example spinodal decomposition in alloys, dendrite formation in melts, martensitic twins in metallic and ceramic alloys, where the assembly process is driven by thermodynamic and kinetic considerations. In this paper, we report on the self-assembly of nanometer-scale hillocks of conducting palladium oxide. We report the formation of almost periodic arrays of self-assembled hillocks upon oxidation of Pd films. The $PdO_2$ hillocks are referred to as "tips" due to their significantly large heights ($\sim 1\mu$m) and conical shape. The tips are spaced $\sim 2.5\mu$m apart and their formation is dependent on the film thickness, granularity and annealing conditions. The height and size of the $PdO_2$ tips increased and their distribution became narrow with increasing film thickness. Photoelectron emission microscopy studies show emission from locations corresponding to the tips. In addition, we present results on the thermal stability of these nanostructures and as well as detailed microstructure studies using high resolution transmission electron microscopy. Also, we demonstrate that these structures can be fabricated on a number of substrates including glass and silicon.

**2:00 PM F5.2**
THIN FILM COMBUSTIBLE GAS SENSORS BASED ON ZINC OXIDE. P. Nunes, E. Fortunato, R. Martins, CENIMAT, Department of Materials Science, Faculty of Sciences and Technology, New University of Lisbon and CEMOP-UNINOVA, Monte de Caparica, PORTUGAL.

Zinc oxide is an important material with many applications in the area of sensors and actuators. The used of zinc oxide thin films as sensitive element in gas sensors as some advantages compared with the traditional tin oxide such as its low cost, high chemical and thermal stability and its etching facility. The sensitivity of zinc oxide thin films is due to the adsorption/desportion phenomena that happens in its surface leading to an increase or decrease in the films resistivity. One of the techniques used to deposit these films is the spray pyrolysis. This technique can be distinguished from the others due to its simplicity, low cost and efficiency. In this paper we present a study on sensitivity (variation of the sensitivity with the gas concentration and testing temperature) of ZnO thin films to several gases such as methane and ethane. We also performance same hall measurement in function of temperature and in the presence of gas with the aim to explained the mechanisms which leads to ZnO thin films sensitivity to combustible gases.

**2:15 PM F5.3**
ELECTRICAL CHARACTERISTICS OF DOPED and UNDOPED HIGH DIELECTRIC CONSTANT BCTZ THIN FILMS. Woo-Chul Yi, T.S. Kalkur, University of Colorado, Colorado Springs, CO; Elliott Philofsky, Lee Kammerdiner, Applied Ceramics Research, Colorado Springs, CO; Tony Rywak, Gennum Corporation, CANADA.

Barium Calcium Titanate Zirconate (BCTZ) materials have high dielectric constant (up to 30,000) in the bulk form. In this paper, we are presenting the electrical and structural characteristics of doped and undoped BCTZ films on oxidized silicon substrates with sputtered titanium/platinum bottom electrode. The BCTZ films were deposited by spin on MOD(metallorganic deposition) and annealed at a temperature 600 -900C in oxygen environment. The annealed films were characterized by x-ray diffraction, scanning electron microscopy and EDAX. The electrical characteristics of the annealed films were annealed by capacitance-voltage(C-V), current-voltage (I-V) and current-time(I-t) measurements. The samples were post annealed in nitrogen and oxygen environments and the effect of post annealing on their electrical characteristics were also presented.

**2:30 PM F5.4**
OXIDE ELECTRODES FOR CUPRATE CHANNEL OXIDE DEVICES. A.G. Schrott, J.A. Misewich, IBM Research Division, Yorktown Heights, NY; R. Ramesh and V. Nagarajan, University of Maryland, Center for Superconductivity Research, College Park, MD.

Perovskite oxides are a class of materials that possess very interesting properties which could open a new field for electronic devices not based on silicon. These oxides exhibit a wide range of behavior depending on chemical composition, temperature, electric fields, and magnetic fields. In order to use these properties for device applications, the development of compatible electrodes and interconnects needs to be accomplished. Some of these oxides, for instance high temperature oxide superconductors and colossal magneto resistance manganates, exhibit contact problems with metal electrodes, which poses a problem for fabricating devices with certain degrees of complexity. In these devices, single crystal quality epitaxial oxide films are used as the superconducting, conducting, or semiconducting layer. The architecture of these complex structures requires a network of buried electrodes present on the substrate during the deposition of the active oxide layers. Therefore, the reactivity and epitaxial compatibility of these active oxide materials with the electrodes is an important parameter relevant to the performance of complex devices. It has been known that some perovskite oxides such as strontium ruthenate (SRO) and lanthanum strontium cobalt oxide (LSCO) provide good contact with PZT made capacitors. In this work we describe a method for making oxide electrodes for structures that require good epitaxial growth and demonstrate its application on epitaxially grown cuprates. [1] V. Nagarajan, I.G. Jenkins, S.P. Alpay, H. Li, S. Aggarwal, L. Salamanca Riba, A.L. Roytburd, and R. Ramesh, J. Appl. Phys. 86, (1999) 595. The work at Maryland is supported by the NSF-MRSEC under grant No. DMR-00-80008

**2:45 PM F5.5**
INHOMOGENEOUS STRUCTURE OF MAGNETIC OXIDES AND TUNNELING DEVICES. Lev Gor'kov, National High Magnetic Field Laboratory, Florida State Univ, Tallahassee, FL; Vladimir Kresin, Lawrence Berkeley Laboratory, Univ of California, Berkeley, CA.

Manganites, which are characterized by a complex phase diagram, are treated as intrinsically inhomogeneous materials. The insulator-metal transitions which occur at a critical concentration (at low temperatures) or at a critical temperature (into the CMR state) are percolation phenomena. A theoretical analysis and an explanation of key experiments will be presented. Various properties of the metallic phase can be described by a two-band model. A new type of spectroscopy employing S-M-S Josephson structures (S is a superconductor, M is a magnetic system) is proposed. The amplitude of the current and its dependence on the external field and on the junction parameters are very sensitive to the magnetic structure of the M compound. This feature also holds promise for various device applications.

**3:00 PM F5.6**
CHARACTERIZATIONS OF THE METAL/FERROELECTRIC/ INSULATOR/SEMICONDUCTOR AND METAL/FERRO-ELECTRIC/METAL/INSULATOR/SEMICONDUCTOR STRUCTURES USING $Pb(Zr,Ti)O_3$ FERROELECTRIC THIN FILMS. Jung-Ho Park, Jang-Sik Lee, and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

In this work, metal/ferroelectric/insulator/semiconductor (MFIS) and metal/ferroelectric/metal/insulator/semiconductor (MFMIS) structures using $Pb(Zr,Ti)O_3$ (PZT) films were fabricated and characterized for nonvolatile NDRO memory device. 300nm-thick PZT films were deposited by reactive RF magnetron sputtering method on $ZrTiO_4$(ZT)/Si and Pt/ZT/Si substrates. C-V hysteresis were measured in both MFIS and MFMIS structures. By using a small-size MFM capacitor on a large-size MIS structure, it was found that the memory window of MFMIS structure was larger than that of the MFIS structure. There is a critical area ratio ($S_{MIS}/S_{MFM}$) in MFMIS structure. When an area ratio in MFMIS structure is below 12, the memory window increased with increasing the area ratio. We could obtain that the memory window of MFMIS structure with a $S_{MIS}/S_{MFM}$ of 11.8 was 2.1 V and 3.2 V with an applied voltage at 3 V and 5 V. The effects of the area ratio on the electrical properties of MFMIS structure will be discussed in detail. The electrical properties of MFMIS structure with different insulator layer are also going to be made.

SESSION F6: FERROELECTRIC MATERIALS I
Chairs: Jeremy Levy and Marilyn E. Hawley
Wednesday Afternoon, April 18, 2001
Salon 3/4 (Marriott)

**3:30 PM *F6.1**
RELATIONSHIPS BETWEEN MICROSTRUCTURE AND RELIABILITY IN PZT MEMS. B.W. Olson, L.M. Randall, C.D. Richards, R.F. Richards, and D.F. Bahr, Mechanical and Materials Engineering, Washington State University, Pullman WA.

Piezoelectric oxide films, such as lead - zirconate - titanate (PZT), are now being integrated into MEMS applications. Many PZT derived systems are deposited using metallorganic precursor process, which can be integrated into a standard microelectronics processing route using spin coating as the deposition method. However, the solution deposition routes can lead to significant residual stresses in the film due to the high processing temperatures required. Variations in processing of both the metallic electrodes and the oxide film itself lead to microstructure changes, including grain size and microcracks. An application of interest for PZT films is in power generation, where a flexing membrane is used to transform mechanical to electrical energy. In this application, the films will be required to deform to strains between 0.1 and 0.5% over several billion cycles. Therefore, the current study was undertaken to identify the relationships between the processing, microstructure, residual stresses, and mechanical reliability of these films. Films were deposited using standard sol-gel chemistries, and residual stresses and grain size has been tracked using contract profilometry as well as electron and scanning probe microscopy. Mechanical properties were evaluated in a dynamic bulge testing apparatus. Grain size variations between 75 and 150 nm are shown to have little effect on film fracture. Fatigues tests show that increased residual stress correlate to decreased film lifetime, but this is primarily due to the increased number of pre-existing flaws in the film. Reducing the microcrack density has been shown to produce films which fail at strains about 1.4%, and have fatigue lifetimes greater than 100 million cycles.

**4:00 PM *F6.2**
OPTIMIZATION OF DIELECTRIC AND STRUCTURAL PROPERTIES OF $Ba_{1-x}Sr_xTiO_3$ FILMS FOR TUNABLE MICROWAVE DEVICES. Q.X. Jia, B.H. Park, B.J. Gibbons, A.T. Findikoglu and Y. Fan, Superconductivity Technology Center, Los Alamos National Laboratory, Los Alamos, NM; Y. Gim, Superconducting Device Group, Jet Propulsion Laboratory, Pasadena, CA; P. Lu, Department of MS&E, New Mexico Tech, Socorro, NM; G.

Wang and X.D. Xiang, Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

Both chemical composition and microstructure have been recognized to play an important role in determining the dielectric properties of $Ba_{1-x}Sr_xTiO_3$ (BST) thin films. In this talk, we will discuss our efforts to optimize the microstructure and dielectric properties of these films via doping and careful process control. This has resulted in development of high performance BST films with a maximized K factor (figure of merit, defined as dielectric-tunability/dielectric-loss). Unfortunately, there is a trade-off between dielectric tunability and dielectric loss. This needs to be considered if one wants to maximize the K factor. We, however, have found that this can be done by carefully manipulating the chemical composition (doping) and the microstructure. For example, we have reproducibly deposited BST films having a dielectric loss of less than 0.001 at 2.22 GHz and a K factor over 60 at a surface electric field of 200 kV/cm and room temperature. These epitaxial BST films have been grown by pulsed laser deposition on MgO substrates. The dielectric properties of these films at both low and high frequencies will be discussed in this talk.

**4:30 PM F6.3**
STRESS EVOLUTION AND FERROELECTRIC PROPERTIES OF PZT THIN FILMS. Maxim Kelman, Paul McIntyre, Stanford University, Dept. of MS&E, Stanford, CA; Jeff Roeder, Bryan Hendrix, Steven Bilodeau, ATMI Inc., Danville, CT.

Ferroelectric and piezoelectric properties of Lead Zirconate Titanate (PZT) thin films make them applicable in a variety of applications including nonvolatile memories, sensors and other MEMS devices. These applications require films of different thicknesses and properties. In this report we will present the thickness dependence of electrical and structural properties of epitaxial and polycrystalline MOCVD grown PZT thin films. High quality epitaxial Lead Titanate (PT) thin films of thicknesses from 100A to 1500A were grown on Strontium Titanate. Rocking curve of the (002) PT peak was determined to be 0.06 degrees for 100A and 360A thick films. Polycrystalline PZT thin films of thicknesses of 700-4000A were grown on iridium bottom electrodes using MOCVD. The composition and structural properties of the epitaxial and polycrystalline films were investigated using a four-circle x-ray diffractometer, atomic force microscopy, Rutherford backscattering spectrometry and high-resolution cross section SEM. We have determined stress evolution in epitaxial and polycrystalline thin films as a function of thickness and processing parameters, as measured by wafer curvature and X-Ray diffraction methods. We will also discuss the evolution of grain size and domain populations in polycrystalline films with thickness and their correlation to electrical properties.

**4:45 PM F6.4**
OXYGEN VACANCY DISTRIBUTION IN PEROVSKITE THIN FILMS AND RELATED ELECTRICAL PHENOMENA. Ralf Liedtke, Rene Meyer and Rainer Waser, Inst. fuer Werkstoffe der Elektrotechnik, RWTH Aachen, GERMANY.

Recently, it has been shown that oxygen vacancies in perovskite thin films alter the electrical properties of metal-perovskite-metal thin film capacitors. In our numerical study a finite-difference based simulation programm (aixpert) was developed in order to calculate the distribution of oxygen vacancies in (Ba,Sr)$TiO_3$ thin films. Due to internal electrical fields which are induced by the metal-perovskite Schottky contact positively charged oxygen vacancies redistribute at elevated temperatures. As an example we will show that for n-type (Ba,Sr)$TiO_3$ thin films oxygen vacancies accumulate at the electrodes which lead to a drastical depletion of electrons in the thin film. Applying an external bias the oxygen vacancies are attracted by the negatively charge electrode. The current density versus elapsed time shows a significant maximum. We compare experimetal data with the simulation results. It is found that the redistribution of oxygen vacancies is mainly responsible for the time dependent leakage current.

## SESSION F7: POSTER SESSION
## TRANSPORT AND MICROSTRUCTURAL PHENOMENA IN OXIDE ELECTRONICS
Chairs: Dave H.A. Blank and David C. Paine
Wednesday Evening, April 18, 2001
8:00 PM
Salon 1-7 (Marriott)

**F7.1**
NIOBATE FILMS FOR MICROWAVES. Choong-Rae Cho, Jung-Hyuk Koh, Alex Grishin, Dept of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN; Saeed Abadei, Spartak Gevorgian, Dept of Microelectronics, Chalmers University of Technology, Göteborg, SWEDEN.

We present comparative analysis of microwave properties of three different niobate films: Na0.5K0.5NbO3 (NKN), AgTa0.38Nb0.62O3, and AgTa0.5Nb0.5O3 (ATN) grown by pulsed laser ablation of stoichiometric ceramic targets onto oxide LaAlO3(001), Al2O3(0-112), and MgO(001) single crystals, low and high resistive Si(001) and Si(111) wafers as well as onto the bulk Pt80Ir20 substrates. Films on the oxide single crystal substrates are single phase, and were found to grow in strict epitaxial relationship with the substrates: exclusively (001) oriented and strongly in-plane textured. NKN films on Si wafers grow as quadrupled structures perfectly oriented along the polar axis. Even on polycrystalline Pt80Ir20 substrates NKN films exhibit strong effect of self-assembling along [001] direction. Rutherford Backscattering (RBS) analyses prove the identity of films and targets composition. To study films properties in a broad frequency band 1 kHz to 50 GHz, planar interdigital capacitors with various gap between electrodes, electrodes shape and length (gap from 2 to 4 um and length up to 1 mm) have been fabricated and characterized. ATN films show moderate losses (tan delta at 1 MHz as low as 0.008 and 0.004 at zero and 200 kV/cm dc bias respectively), weak frequency dispersion of the dielectric constant, Q-factor, and tunability about 10% @ 200 kV/cm in a whole range up to 50 GHz. NKN films on highly resistive (7.7 kOhm cm) SiO2/Si substrate at 40 GHz show Q-factor > 15 and tunability @ 100 kV/cm as high as 13%. We conclude niobate films have great potential for applications in low loss electrically tunable microwave and millimeter wave devices.

**F7.2**
INTEGRATION OF BIAXIALLY ALIGNED $SrRuO_3$ AND $Sr_2RuO_4$ WITH SILICON USING AN IBAD-MgO INTERMEDIATE LAYER. Luke A. Emmert, Bae-Ho Park, J. Randy Groves, Raymond F. DePaula, Quanxi Jia, and Paul N. Arendt, Superconductivity Technology Center, Los Alamos National Laboratory, Los Alamos, NM.

Biaxial alignment of pseudocubic perovskite $SrRuO_3$ and layered perovskite $Sr_2RuO_4$ deposited on silicon substrates by pulsed laser ablation will be demonstrated. Amorphous silicon nitride protects the underlying silicon from any reaction during the oxide processing. Biaxial alignment is achieved on this amorphous surface in a 100 Å film of MgO using ion-beam-assisted depostion (IBAD). The cubic perovskite phase exhibits unwanted (110) as well as (111) texture when deposited directly on the IBAD layer. Including a homoepitaxial MgO layer reduces these unwanted orientations. X-ray pole-figure data will be presented correlating the MgO alignment with the final mosaic spread of the perovskites.

**F7.3**
THE DEPENDENCE ON PLASMA IN PULSED LASER DEPOSITION FOR THE SURFACE PASSIVATING QUALITY OF OXIDES ON SILICON. Lianne Doeswijk, Arjen Janssens, Peter Laloli, Dave Blank, Horst Rogalla, University of Twente, Dept. of Applied Physics, Low Temperature Division, Mesa, Enschede, NETHERLANDS.

We are exploring the possibilities of introducing passivating qualities in oxide coatings. Stoichiometric oxides ($TiO_2$, $SrTiO_3$, $BaTiO_3$) show no passivating qualities. Introduction of positive oxide charge in the coatings by deposition in an oxygen deficient ambient, results in increased surface passivation. The introduction of water vapour in the vacuum chamber results in a further increase in surface passivation. However, the best result is obtained by deposition of reduced $TiO_{2-x}$ with the substrate (at room temperature) placed perpendicular to the target. Altering these deposition parameters changes the plasma characteristics. A study has been made on the visible changes in the plasma as function of deposition parameters and the effect on measured surface passivation. Also, we explored the deposition of oxides in the perpendicular set-up. With the use of 3" silicon wafers we could measure the achieved surface passivation as function of the position in the plasma. To unravel why coatings show surface passivation, effort is undertaken to determine the extent and content of the interface between the coating and silicon substrate.

**F7.4**
PHASE FORMATION KINETICS IN SOL-GEL DERIVED STRONTIUM BISMUTH TANTALATE. Yun-Mo Sung, Woo-Chul Kwack, Daejin University, Dept of Materials Science & Engineering, Pochun-koon, Kyunggi-do, KOREA (SOUTH).

$Sr_{0.7}Bi_{2.4}Ta_2O_9$ (SBT) powder was synthesized via sol-gel and pyrolysis process and analyzed for phase formation kinetics. Each of the two exotherms, appearing in differential thermal anlaysis (DTA) scan curves, was identified as crystallization of fluorite phase and transformation of fluorite to aurivillius phase, respectively. By applying non-isothermal kinetic analyses to the DTA results, activation energy values for the formation of fluorite and aurivillius phases were determined as 192 and 375 kJ/mol, respectively and Avrami exponent vlaues for the reactions were determined as 0.91 and

0.96, respectively. These activation energy and Avrami exponent values were discussed in detail to understand phase formation mechanism in SBT system.

**F7.5**
KINETIC ANALYSIS OF $PbTiO_3$ PHASE FORMATION VIA DIFFUSION COUPLE METHOD. Yun-Mo Sung, Woo-Chul Kwack, Daejin Univ, Dept of MS&E, Pochun-koon, Kyunggi-do, KOREA (SOUTH).

A detail kinetic analysis was performed on the $PbTiO_3$ phase formation reaction occurring via PbO-$TiO_2$ diffusion couple experiments. The diffusion model of $Pb^{2+}$ and $O^{2-}$ ions was used to derive the kinetics equation of the $PbTiO_3$ phase formation reaction. From the parabolic kinetics between the thickness of the $PbTiO_3$ layer and time, the reaction rate constant for the $PbTiO_3$ phase formation was determined to be a function of the average diffusion coefficient of $Pb^{2+}$ ions. By substituting the diffusion couple results into the present kinetics equation, average diffusion coefficient values of $Pb^{2+}$ ions in $PbTiO_3$ layer were calculated according to temperature values. The activation energy value for the diffusion of $Pb^{2+}$ ions in $PbTiO_3$ layer was estimated using Arrhenius plot and the equation for the diffusion coefficient of $Pb^{2+}$ ions was also determined.

**F7.6**
MANIPULATING THE NUCLEATION AND GROWTH OF REBaCuO. Guus Rijnders, Dave Blank, Horst Rogalla, University of Twente, Low Temperature Division, MESA Research Institute, Enschede, THE NETHERLANDS; Sara Bals, Gustaf van Tendeloo, EMAT-RUCA, Antwerp, BELGIUM.

The nucleation and growth of the cuprate high Tc materials, especially the REBaCuO compound, have been subject to many studies in the last ten years. In the case of deposition techniques such as pulsed laser deposition (PLD) or sputter deposition especially the growth mode was studied. Depending on the growth conditions, a multiple level 2D growth or spiral growth have been observed. As a consequence, the surface of the film is roughened. Starting with an atomically smooth substrate, i.e., titanium dioxide terminated strontium-titanate, we studied the growth of REBaCuO using high-pressure RHEED. Using standard PLD conditions, nucleation of sub-unitcell blocks during the initial growth is observed by AFM and TEM. As a consequence, defects such as anti-phase-boundaries, are present in the film. Using pulsed laser interval deposition we have grown YBaCuO films by alternately depositing 2 unit cell layers of BaCuO and 1 unit cell layer of YCuO. Using this artificial deposition method we obtained superconducting films with a smooth surface morphology. Only step heights smaller than the c-axis length of YBaCuO have been measured by AFM.

**F7.7**
STRUCTURAL AND ELECTRICAL PROPERTIES OF $Y_2O_3$ BUFFER LAYER BY TWO-STEP PROCESS. Dong-Gun Lim, Bum-Sik Jang, Sang-il Moon, Junsin Yi School of Electrical and Computer Engineering, Sungkyunkwan University, Jangan-gu, Kyunggi-do, KOREA.

In this paper we investigated a feasibility of $Y_2O_3$ films as a buffer layer of MFIS ferroelectric transistor. Buffer layers were prepared by two-step processes using a low temperature film growth and subsequent RTA treatment. Investigated parameters are substrate temperature, $O_2$ partial pressure, post-annealing temperature, and suppression of interfacial $SiO_2$ layer generation. By employing an ultra thin Y pre-metal layer, unwanted $SiO_2$ layer generation was successfully suppressed at an interface between the buffer layer and Si substrate. With the elevation of the post-annealing temperature, surface roughness of $Y_2O_3$ films was reduced. And as increasing the $O_2$ partial pressure, surface roughness was increased. The $Y_2O_3$ films annealed at 900°C and with 20% $O_2$ partial pressure exhibited the best surface roughness characteristics. With RTA treatment, we improved the leakage current density of $Y_2O_3$ films about 2 orders and the $D_{it}$ as low as $8.72\times10^{10}$ cm$-2\cdot$eV$-1$. Substrate temperature above 400°C or $O_2$ partial pressure of 20%, the monoclinic $Y_2O_3$ film structure was disappeared and the cubic $Y_2O_3$ phase was dominated in XRD spectra. And we achieved low lattice mismatch of 1.75%. We recommend that $Y_2O_3$ buffer layer for a single transistor FRAM should be grown at 400°C with 20% $O_2$ partial pressure then RTA treatment at 900°C in oxygen ambient.

**F7.8**
NANO-SCALE INTERFACIAL REACTIONS OF $SrRuO_3$ THIN FILM ON Si (100) SUBSTRATE. Sang Ho Oh, Chan-Gyung Park, Pohang Univ of Sci and Tech (POSTECH), Dept of Materials Science and Engineering, Pohang, KOREA.

Interfacial reactions and defects of the $SrRuO_3$ thin film grown on Si substrate by ion beam sputtering have been investigated by using field emission-transmission electron microscopy (FE-TEM). The objective of the present study is to investigate structural and chemical variations of the nano-scale reaction layers between Si and $SrRuO_3$, which can result in the understanding of reaction thermodynamics of $SrRuO_3$ and Si contact system. The $SrRuO_3$ films grown on Si substrate revealed no preferred orientation regardless of the change in growing conditions, such as growing temperature and oxygen pressure. It was found that the interfacial reactions occurred at the initial stage of the growth was the major cause of the random growth behavior. According to morphology and composition analyzed, the reaction layers between Si and $SrRuO_3$ were identified as the following four different layers: 1) Sr-Si-O layer, 2) amorphous $SiO_2$ layer, 3) Sr-Si-O layer, and 4) nano-sized Ru-rich grains containing Si and O. The nano-sized Ru-rich grains were revealed to be elemental Ru with hexagonal structure. The reaction layers and their characteristics could be explained by considering the chemical reactivity of the binary constituent oxides of $SrRuO_3$, SrO and $RuO_2$, with Si substrate. That is, the SrO can be stable in contact with Si because Sr-Si-O ternary system has a stable tie-line between SrO and Si. However, the $RuO_2$ can not be stable with Si, because Ru-Si-O ternary system has a stable tie-line between not $RuO_2$ and Si but Ru and $SiO_2$. The reduction of $RuO_2$ constituent oxide into elemental Ru by Si is believed to the most favorable candidate reaction, which can lead to unstable contact of $SrRuO_3$ on Si. Based on the structural and chemical information of reaction layers analyzed and with thermodynamical calculation, possible reaction thermodynamics of $SrRuO_3$ and Si contact system is proposed as $SrRuO_3$ Si $\rightarrow$ SrO Ru $SiO2_2$ ($\Delta G_{1000K} \approx$ -762kJ/mol).

**F7.9**
EFFECTS OF PRE-HEAT TREATMENT ON THE CRYSTALLIZATION AND CHARACTERISTICS OF ION-TREATED $SrBi_2(Ta,Nb)_2O_9$ (SBTN) THIN FILMS. Jang-Sik Lee and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

Ferroelectric random access memories (FRAMs) are being developed extensively. One of the most promising ferroelectric materials for use in FRAMs is the bismuth layered perovskite $SrBi_2(Ta,Nb)_2O_9$ (SBTN). In this work, we will present pre-annealing effects on the phase transformation of SBTN thin films with and without ion treatment. Details about the ion treatment method will be presented at this MRS meeting. [1] Ferroelectric SBTN thin films were fabricated by metal-organic decomposition method. Effects of pre-rapid thermal annealing temperature on the crystallization behavior and the electrical properties of SBTN thin films were investigated. The higher the preannealing temperature is, the lower the crystallization temperature is. It was found that the electrical properties of the SBTN thin films processed at high preannealing and low post annealing temperature were almost the same as those of SBTN thin films fabricated at low preannealing and high post annealing temperature. However, interesting results were obtained when the films were ion-treated before post annealing, that is the lower the preannealing temperature is, the lower the crystallization temperature is. Thus, there exist optimized preannealing temperature and ion treatment to obtain SBTN thin films with high quality and low processing temperature. In this presentation, the effects of preannealing temperature on the phase transformation and ferroelectric characteristics of SBTN thin films will be discussed in detail. The correlation between the ion treatment and heat treatment temperature in SBTN thin film process is also going to be presented. [1] J.-S. Lee and S.-K. Joo, "Low temperature processing and characterization of ferroelectric thin films by ion pre-treatment method".

**F7.10**
ZINC FERRITE THIN FILMS PREPARED BY MOCVD, WITH DENDRITE STRUCTURE OBSERVED. Yuneng Chang, Ginwen Wang, Zeyin Lin, Lunghwa Inst. of Tech., Dept of Chemical Engineering, Gueishan, Taoyuan, Taiwan, ROC.

In this research, we chose MOCVD technique to deposit spinel ferrite thin films. Since in MOCVD process, metal elements, which constitute oxide ceramic films, appear as individual surface adatoms, and being transported by surface diffusion to form solid product. The activation energy of such process is much less than the activation energy of bulk diffusion required for conventional sintering. Thus MOCVD could be used to prepare crystalline ceramics at lower temperatures, and be more suitable for device used ferrite thin film manufacturing. Ferrite films were deposited in a horizontal cold wall APMOCVD system; with precursors zinc acetylacetonate and iron acetylacetonate heated, vaporized, and transported by $N_2/O_2$ mix carrier gas onto the gas boundary layer above Si substrate surface. With deposition temperature between 400°C and 440°C, normal spinel zinc ferrite ($ZnFe_2O_4$) films were produced. XRD patterns, together with AES/XPS results, show the primary crystalline phase being $ZnFe_2O_4$ (311). SQUID results show that films were antiferromagnetic, with

magnetic parameters such as coercive field (Hc), permeability ($\mu$), saturation magnetization (Ms), and remanece magnetization (Mr) measured. SEM micrographs indicated that oxygen concentration was a determining factor to film microstructure and morphology. The deposited $ZnFe_2O_4$ films exhibited an interlocking dendrite network for process oxygen concentration above 30%, but showed fine grain/smooth surface for oxygen concentration below 15%. The primary arm length of some dendrites achieved 10$\mu$m, with secondary arm length 2-0.5$\mu$m. The average dendrite arm spacing was 1$\mu$m. Due to the large specific surface area, high surface energy, and thermodynamically unstableness own by dendrites, their appearance was taken as evidences and caused us assumed this CVD was controlled by kinetics, rather than thermodynamics. Based on Lewis' and Doherty's theories, we have postulated a simplified conceptual model describing $ZnFe_2O_4$ dendritic growth kinetics. An optimized process window will also be discussed in this presentation.

**F7.11**
RANDOM TELEGRAPH LIKE SIGNALS IN ULTRA-THIN CMR FILMS. A. Lisauskas, S.I. Khartsev, A.M. Grishin, Dept of Physics, Sect of Condensed Mater Physics, Royal Institute Of Technology, Stokholm, SWEDEN.

In recent work we have shown that material properties of thin films colossal magnetoresitors can be effectively tailored with decreasing of thickness below the critical one [1]. Here we present results on low frequency (10 Hz $\div$ 10 kHz) noise spectroscopy, which yields additional information relating to the spin dependent electron transport in structures with reduced dimensionality. Two contributions in electrical fluctuations were observed: thermal noise, which depends on resistance and temperature, and excess part, which is determined by resistance fluctuations and are mostly related to film microstructure. For films, thicker than critical thickness, excess noise spectra has $1/f^{\alpha}$ dependence with $\alpha = 1 \pm 0.2$. In films with thickness below the critical one, in addition to $1/f$ noise random telegraph like signals (TLS) with Lorentzian spectra appear. Fitting of noise spectra measured at different temperatures revealed relaxation time constant, which decreases with the temperature increase. Different mechanisms responsible for TLS in low-dimensional CMR films will be discussed and compared with the experimental data. [1] S. I. Khartsev, P. Johnson, and A. M. Grishin, J. Appl. Phys. 87. 2394 (2000).

**F7.12**
COLOSSAL TEMPERATURE COEFFICIENT OF REESITIVITY IN EPITAXIAL COLOSSAL MAGNETORESISTIVE LCMO FILMS. S.I. Khartsev and A.M. Grishin. Dept of Physics, Sect of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN.

Thin manganite perovskite films have been considered as promising candidates for uncooled and moderately cooled bolometers due to presence of sharp insulator-to-metal phase transition. Such applications require the temperature coefficient of resistivity (TCR = $1/RdR/dT$) to be high close to operating temperature. At the same time magnitude of TCR shows how narrow the phase transition indicating film performance, phase and structure homogeneity. Our results obtained for different CMR compositions and substrates show that increase of the peak value of TCR results in magnetoresistivity increase, since magnetoresistive effect occurs due to the shift of $R$ vs. $T$ dependence to higher temperatures at applied magnetic field. Therefore, even small shift of the sharp $R-T$ curve results in appearance of essential magnetoresistivity. We chose widely explored $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) composition to get superior TCR by optimization processing parameters and film-to-substrate crystalline affinity. LCMO films have been fabricated by KrF ecximer PLD process. Three different (001) oriented single crystals were used as substrates: $LaAlO_3$ (LAO), $SrTiO_3$ (STO), and $NdGaO_3$ (NGO) having film-to-substrate mismatch 1.26%, -0.9% and 0.18% correspondingly. Independently on deposition parameters the best film performance was achieved for substrate with a minimum mismatch to LCMO film. For example, at substrate temperature of 800°C, oxygen pressure of 250 mTorr and laser fluency of 3 J/cm$^2$ we have obtained the following transition temperature and TCR: 272 K and 9.44 %/K @ 253 K for NGO, 252 K and 6.9 %/K @ 235 K for LAO, and 237 K and 7.1 %/K @ 207 K for STO. We choose NGO substrate as the basis for technological quest. We found that the highest TCR of 21%/K @ 247 K can be obtained at moderate substrate temperature around 700°C. Following *ex-situ* postanneling of such structure brings TCR to record value of 35%/K @ 266 K. This is more than two times higher than TCR whenever reached. This film demonstrates magnetoresistance of 65% @ 268 K & 7 kOe.

**F7.13**
CHEMICAL DIFFUSION BARRIERS FOR SUPERCONDUCTING COATED CONDUCTORS. G. Koster, W. Jo, T.H. Geballe, M.R. Beasley, R.H. Hammond, Theodore H. Geballe Laboratory for Advanced Materials, Stanford University, Stanford, CA; R. Feenstra, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN; M. Huijben, Mesa, University of Twente, THE NETHERLANDS; R.E. Ericson, 3M Company, St. Paul, MN.

We investigate the possibility of using chemical diffusion barriers on metal tape substrates for biaxially aligned $YBa_2Cu_3O_{7-\delta}$ thick films. At the fast deposition rates and high temperatures used to process these thick films a very reactive growth interface is expected. Especially the element Ba is known to diffuse and react chemically with the constituents of the metal (alloy) thereby causing non stoichiometry in the film. In order to prevent this from happening we are looking for a material to both withstand high temperatures and be chemically inert for film and substrate. $BaZrO_3$ has been used successfully as crucible material for single crystal growth of $YBa_2Cu_3O_{7-\delta}$. The remarkable quality of these crystals has been attributed to the inertness of $BaZrO_3$ towards $YBa_2Cu_3O_{7-\delta}$. Therefore, we think that $BaZrO_3$ is a suitable candidate to act as a chemical diffusion barrier provided that it can be grown with reasonable crystallinity and a smooth surface. In this paper we discuss the properties of our $BaZrO_3$ thin films grown on a variety of substrate materials, both single crystalline as well as metal tapes, by pulsed laser deposition. In addition, we have focussed our research to get to fully stoichiometric films. RBS showed a low minimum yield of 1-3% in ion channeling for a $BaZrO_3$ layer (on STO) that appeared to be close to the ideal stoichiometry (i.e., Ba:Zr=1:1).

**F7.14**
CHARACTERIZATION OF La-Sr-Mn-O THIN FILMS DEPOSITED ON SINGLE CRYSTAL SUBTRATES. Lamartine Meda, LaQuita Kennon, and Hamid Garmestani, FAMU-FSU College of Engeneering, MARTECH, CeNNas and The National High Magnetic Field Lab, Tallahassee, FL; Klaus H. Dahmen, Dept Chemistry, The Florida State University, FL.

Thin films of $La_{1-x}Sr_xMnO_3$ (LSMO) were prepared at 670°C on LAO(100), STO(100), and MgO(100) single crystal substrates by liquid-delivery metal-organic chemical vapor deposition (LD-MOCVD). X-ray diffraction (XRD) $2\theta$-$\theta$ and pole figure scans showed that the films are highly texture with LSMO(001)//LAO(001), LSMO(001)//STO(001), and LSMO(001)//MgO(001). Electron microscopy revealed square facets and elongated grain features. Films heat-treated between 700 - 1000°C on LAO undergo some structural changes, while those on STO showed little change in texture.

## SESSION F8: FERROELECTRIC MATERAILS II
Chairs: David L. Young and Chang Beom Eom
Thursday Morning, April 19, 2001
Salon 3/4 (Marriott)

**8:30 AM *F8.1**
PHYSICAL ORIGINS OF MICROWAVE DIELECTRIC LOSS IN FERROELECTRIC THIN FILMS. Jeremy Levy, Charles Hubert and Oleg Tikhomirov, University of Pittsburgh, Dept of Physics and Astronomy, Pittsburgh, PA.

A number of spatially and temporally resolved probes of ferroelectric thin films have been developed, with the principal goal of determining the fundamental mechanisms for microwave dielectric loss. From these experimental investigations has emerged a consistent picture that links the increased dielectric loss of thin films to inhomogeneous broadening of the ferroelectric phase transition. We have recently performed the first direct measurements of local ferroelectric phase transitions in (Ba,Sr)$TiO_3$ thin films; these measurements show that the local phase transition is more than an order of magnitude sharper than the inhomogeneously broadened peak obtained from standard dielectric measurements. Because the dielectric loss depends strongly on (T-Tc), there will inevitably be local regions which exhibit large dielectric loss. These conclusions are supported by spatially resolved microwave measurements of the ferroelectric polarization. Mechanisms for both tuning and loss are described in terms of reorientation of nanopolar regions for interdigitated electrode geometries, the ability to reorient polarization from out-of-plane to in-plane is associated with high dielectric tuning, while the strength of the linear electrooptic response at zero bias is correlated with dielectric loss. A much higher spatial resolution probe is under development that will allow microwave dynamics to be resolved with a spatial resolution smaller than the grain size ($\sim$50 nm). This work was supported by the Office of Naval Research (N00173-98-1-G011) and the National Science Foundation (DMR-9701725).

**9:00 AM F8.2**
MOCVD (Ba,Sr)$TiO_3$ THIN FILMS: PROCESSING ISSUES FOR ACTIVE AND PASSIVE DEVICES. D.Y. Kaufman, J. Im, S.K. Streiffer, R.A. Erck, and O. Auciello, Energy Technology Division and Materials Science Division, Argonne National Laboratory, Argonne, IL.

$(Ba,Sr)TiO_3$ thin films have been fabricated for both frequency-agile electronics and passive capacitor circuit elements. The electrical characteristics of each device impose unique processing requirements in such issues as substrates and electrodes, film composition, deposition conditions, and post-deposition processing. Liquid delivery metalorganic chemical vapor deposition has been used to deposit $(Ba,Sr)TiO_3$ thin films on Pt electroded Si and quartz substrates. The effects of Ba:Sr ratio, Ti composition, deposition conditions, and post-annealing on electrical properties such as permittivity, dielectric loss, tunability, and energy density were examined. Tunabilities as high as 2.5:1 with dielectric losses as low as 0.002 have been obtained, as well as energy densities as high as 31 $J/cm^3$. Additionally, BST thin films were deposited on Ni, Hastelloy, and Inconel foils. The role of processing effects on electrical performance, including buffer layers to prevent oxidation and diffusion during growth and processing, were examined. Dielectric constants as high as 400 with breakdown fields of 2 MV/cm have been obtained. *Work supported by the U.S. Department of Energy, Offices of Transportation Technologies and BES-Material Sciences, under Contract W-31-109-ENG-38, and by DARPA, Contract 978040.

**9:15 AM F8.3**
COMPOSITIONAL AND OXYGEN TRANSPORT STUDIES OF ULTRATHIN Zr-Al-Si-O HIGH-K GATE DIELECTRICS.
Brett Busch, Hartmut Schulte, Sudha Aravamudhan, Torgny Gustafsson, Eric Garfunkel, Rutgers University, Depts of Physics and Chemistry, Piscataway, NJ; Martin Green, Mark Morris, Lalita Manchanda, Bell Laboratories, Murray Hill, NJ.

Ultrathin ($\leq$ 5 nm) Si-doped zirconium-aluminates (dielectric constant $\sim$ 20) have been grown on Si(100) by sputtering from a $Zr_{0.78}Al_{0.20}Si_{0.02}$ target. Films have been produced using different sputtering and oxidizing processes: (1) metal sputtering onto clean Si followed by room temperature oxidation in air, (2) metal sputtering followed by *ex-situ* RTO, (3) metal sputtering followed by reactive oxygen sputtering, and (4) reactive oxygen sputtering only. The thickness and stoichiometry of the films (including thickness and composition of interface layers between the high-K film and the Si substrate) were determined by high-resolution medium-energy ion scattering (MEIS). Films produced by reactive sputtering (processes 3 and 4) exhibit a thick (1 – 2 nm) interfacial layer that contains Si, Al and O. Such a deleterious oxide layer is significantly reduced by performing oxidation *ex-situ* after metal deposition (processes 1 or 2). Such films, after oxidation in air at room temperature, are slightly oxygen deficient and show an uptake of Si into the film along with formation of a silicide layer near the interface to the Si substrate. Subsequent RTA in an oxygen containing atmosphere at 450°C (process 2) leads to oxidation of the silicide layer, leaving a thin ($\leq$ 0.4 nm) $SiO_2$ region (possibly containing some metal). Details on oxygen transport (including oxygen exchange and interfacial growth) have been studied with MEIS depth profiling combined with isotopic labeling. Films produced by processes 1 and 2 have been reoxidized in isotopically pure $^{18}O_2$ using different experimental parameters. Substantial $^{18}O$ incorporation was seen at temperatures as low as 400°C. Two regions of oxidation are of interest: oxygen exchange within the high-K film, and oxidation of the silicide layer followed by continued interfacial $SiO_2$ growth. The MEIS results will be correlated to TEM and electrical measurements to obtain a more complete picture of the film characteristics.

**9:30 AM F8.4**
PHASE-FIELD SIMULATION OF PHASE TRANSITIONS AND DOMAIN STRUCTURE EVOLUTION IN FERROELECTRIC THIN FILMS.
Yulan Li, Shenyang Hu, Zikui Liu, Long-Qing Chen, Penn State University, Dept of Materials Science and Engineering, PA.

An efficient method for obtaining the elastic solution of a 3D thin film with arbitrary eigenstrain distributions is proposed. The solution makes it possible to apply phase-field approach to modeling coherent microstructure evolution in a thin film. As an application, the phase-field model is employed to model the domain structure evolution in ferroelectric thin films constrained by a substrate. We employed the conventional Ginzburg-Landau theory to describe the local free energy density and the gradient energy. The elastic solution with a given set of electrostrictive coefficients and substrate constraint is obtained by properly taking into account the free boundary condition on the surface and the constraint boundary condition in the substrate. In particular, the domain structure evolution during a cubic-tetragonal ferroelectric phase transformation is studied by solving the time-dependent Ginzburg-Landau equation using a spectral method. The proposed model is able to predict not only the volume fractions of various orientation domains (for example, a- and c- domains for a tetragonal ferroelectric phase), but also the temporal evolution of domain structures under a given temperature and substrate constraint. With all the model parameters obtained from independent experimental measurements, it is shown that the predicted volume fractions of domain variants, domain-wall orientations, and domain shapes agree very well with existing experimental observations on PZT films on STO substrate. The effect of different substrate constraints and film thickness on the domain structures will be discussed. Work supported by NSF and Penn State Materials Research Institute.

**9:45 AM F8.5**
MICROSTRUCTURAL AND PHYSICAL CHARACTERIZATION OF FERROELECTRIC-GATE MEMORY CAPACITORS WITH VARIOUS BUFFER LAYERS.
Christine Caragianis-Broadbridge, Daniel L. Pechkis, Southern Connecticut State University, Department of Physics, New Haven, CT; Jin-ping Han, Wenjuan Zhu, Zhijiong Luo and T.P. Ma, Yale University, Department of Electrical Engineering, New Haven, CT.

Ferroelectric (FE) thin films have great potential for nonvolatile memory and DRAM applications. Recently, the FE-gate transistor structure has received much attention. The successful fabrication of a ferroelectric-gate transistor structure is largely dependent on the ability to form a high-quality buffer layer between the ferroelectric layer and the underlying silicon substrate. The purpose of the buffer layer is to prevent intermixing between the ferroelectric material and the underlying silicon, and to prevent oxidation of the silicon surface during subsequent processing steps. A suitable buffer layer must also provide an acceptable electronic interface with the silicon substrate. During this study the microstructural and physical properties of Ferroelectric-Insulater-Semiconductor structures prepared utilizing several different buffer layers were evaluated. Specifically, the samples were prepared by depositing $SrBi_2Ta_2O_9$ (SBT) on Si substrates that were first coated with a buffer material. The buffer layers chosen for comparison were: jet-vapor-deposited silicon nitride layer, zirconium silicate, halfnium oxide and a thermally grown silicon oxide layer. For electrical evaluation, metal top and bottom contacts were utilized. For surface and interface characterization, non-contact atomic force microscopy (AFM) and electron microscopy (planview and cross-sectional) data were obtained. Energy Dispersive Spectroscopy (EDS), X-Ray Diffraction (XRD) analysis, and X-ray Photoelectron Spectroscopy (XPS) were utilized for elemental, crystallographic, and chemical evaluation. Capacitance-Voltage (C-V) measurements were used to correlate microstructure and physical properties with memory effects. The results of this study indicate that the final microstructure of deposited ferroelectric SBT film is dependent on the type and quality of the buffer layer. Similarly, memory effects for MFIS structures are impacted by the properties of the buffer material employed.

**10:15 AM F8.6**
FABRICATION AND ELECTRICAL PROPERTIES OF SELF-ASSEMBLED FERROELECTRIC NANOSTRUCTURES.
M. Alexe, A. Visinoiu, C. Harnagea and D. Hesse, Max Planck Institute of Microstructure Physics, Halle, GERMANY.

We have used both main approaches employed in nanotechnology to create nanometer structures: the classical "top-down" approach based on electron-beam lithography, and the "bottom-up" which develops self-assembly methods. The "top-down" approach is an electron beam direct writing method and allows fabrication of ferroelectric $Pb(Zr,Ti)O_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) nanosize structures with lateral sizes under 100 nm. Alternatively, nanosize ferroelectric structures have been prepared using "bottom-up" approaches employing self-assembly fabrication methods based on chemical solution deposition (CSD) and pulsed laser deposition (PLD). In this way PZT and $BaTiO_3$ structures having lateral sizes from 20 nm to 60 nm were prepared on $SrTiO_3$:Nb. Ferroelectric, piezoelectric and switching properties were studied using scanning probe microscope (SPM) working in piezoresponse mode. The same SPM setup with conductive tips was used to measure leakage current in nanosize structures. Electronic transport mechanism in nanosize structures was found to be space charge limited (SCL)-type, i.e. $J(V) = aV^3$, unlike in the case of large-area devices of the same material which is Schottky-dominated.

**10:30 AM F8.7**
FIRST STEP TOWARDS $SrTiO_3$-Si INTEGRATION: STRUCTURAL, CHEMICAL, AND ELECTRONIC PROPERTIES OF STRONTIUM SILICIDE AND STRONTIUM SILICATE ON Si(001).
Y. Liang, S. Gan, V. Vaithiyalingam, S. Thevuthasan, Pacific Northwest National Laboratory, Richland, WA.

Recent work showed crystalline oxides such as $SrTiO_3$ (STO) is promising as an alternative to $SiO_2$ in MOSFET. One of the most important issues in this approach is the interfacial template layer that needs to possess favorable structural and chemical properties for growth of crystalline STO on Si. Here we present our recent results on the study of the oxide-silicon interface. Using scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS),

low-energy electron diffraction (LEED), and Rutherford back scattering (RBS), we investigated the interfacial structure of each template layer (Sr and SrO) grown on Si in situ. It was found that the strontium-covered surfaces exhibit a series of reconstructions depending on the surface strontium coverage. These phases not only had different atomic structures but also different reactivity against oxygen. For instance, upon exposure to oxygen, the (3x2) structure was converted to a disordered (1x1) surface while the (1x2) surface remained intact. For the growth of oxides, the (1x2) structure was found to provide the most stable interface, as evidenced by a uniform layer in angular dependence XPS results, and the lack of interfacial $SiO_2$ layer. In addition to the favorable structural properties and chemical stability, XPS also indicated a reduction of band-bending for the (1x2) layer, suggesting this interfacial template layer was electronically favorable for the removal of gap states at the Si/STO interface. By combining results obtained from STM, XPS, RBS, and LEED, we correlated the interface structures with film properties, which allowed us to identify suitable interfacial templates for optimized growth of STO.

**10:45 AM F8.8**
DOMAIN STRUCTURE IN $LaFeO_3$ THIN FILMS AND ITS ROLE ON EXCHANGE COUPLING. Jin Won Seo[a,b], Jean Fompeyrine[b], Heinz Siegwart[b], Jean-Pierre Locquet[b]; [a]Institute de Physique, Université de Neuchütel, Neuchütel, SWITZERLAND; [b]IBM Research Division, Zurich Research Laboratory, Rüschlikon, SWITZERLAND; Andreas Scholl, Frithjof Nolting, Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA; Jan Lüning, Joachim Stöhr, Stanford Synchrotron Radiation Laboratory, Stanford, CA.

Antiferromagnetic (AF) materials are essential elements in the read-heads of current hard-disk drives, where they serve to pin the nearest ferromagnetic (FM) layer into one preferred orientation. This coupling between the spins in the AF and FM layers-also called the exchange bias-determines to a large extent the efficiency and the long-term stability of the giant magnetoresistance ratio, but is still a poorly understood phenomenon. However, a number of experiments and theoretical models have suggested that the exchange bias is correlated with the presence and morphology of AF domains. The AF orthoferrite $LaFeO_3$ is an interesting AF model system to explore this correlation, as the easy axis A is uniquely defined along the a-axis of the orthorhombic crystal (a = 0.5557 nm, b = 0.55652 nm, and c = 0.78542 nm). The orthorhombicity of this crystal is large enough that its structural recognition on a local scale allows a direct determination of the AF axis. By means of photo-emission electron microscopy AF domains have been found in $LaFeO_3$ thin films grown on $SrTiO_3$ substrates [1]. Growing a thin polycrystalline Co-layer on top of $LaFeO_3$ the correlation between AFM and FM layer could be imaged. The results imply that the alignment of FM spins is determined by the spin directions in the underlying AF layer within an individual domain [2]. In average, smaller domains lead to higher exchange bias. As observed by transmission electron microscopy the AF domains of $LaFeO_3$ are strongly correlated to structural domains. Firstly we study the parameters such as growth condition, epitaxial relationship and strain which control the domain size and shape as well as the Néel temperature. Secondly, we investigate how these parameters effect on the exchange bias. [1] A. Scholl et al., Science 287 (2000) 1014-1016. [2] F. Nolting et al., Nature 405 (2000) 767-769.

**11:00 AM F8.9**
LOW TEMPERATURE PROCESSING AND CHARACTERIZATION OF FERROELECTRIC THIN FILMS BY ION PRE-TREATMENT METHOD. Jang-Sik Lee and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

Ferroelectric memories are novel types of memories especially suitable for mobile applications due to their excellent properties, such as non-volatility, small cell size, fast reading and writing time and low power consumption. However, several issues still require attention for the integrations of ferroelectric materials with existing Si technology. The most important problem is the limitation in the maximum processing temperature. In this work, we will present a novel method for the crystallization of ferroelectric thin films with low thermal budget. Ferroelectric $Pb(Zr,Ti)O_3$ (PZT) and $SrBi_2(Ta,Nb)_2O_9$ (SBTN) thin films were prepared by reactive sputtering and metal-organic decomposition method, respectively. Effects of Ar ion shower prior to the phase transformation of PZT and SBTN thin films have been investigated in terms of ion acceleration voltage and ion treatment time. As the degree of ion treatment increased, the phase transformation temperature decreased. As a result, the crystallization temperature could be lowered down to 550°C for PZT and 650°C for SBTN when the films were pre-treated at 15 kV. It turns out that relatively good electrical properties even at low annealing temperature are closely related to degree of ion treatment and the ion shower technique can be applied to the process of ferroelectric films regardless of their fabrication method. In this presentation, the effects of ion acceleration voltage and time on the crystallization temperature and characteristics of PZT and SBTN thin films will be discussed in detail. The comparison of crystallization behavior and electrical properties between the films with and without ion-treatment is also going to be presented.

**11:15 AM F8.10**
SUBSTRATE INFLUENCE ON THE REVERSIBLE AND IRREVERSIBLE POLARIZATION PROCESSES IN FERROELECTRIC THIN FILMS. D. Bolten, U. Boettger, M. Grossmann, O. Lohse, R. Waser, IWE II, University of Technology Aachen, GERMANY.

In this contribution, the influence of different substrates and textures on the reversible and irreversible polarization in $Pb(Zr,Ti)O_3$ (PZT) thin films will be presented. One possible scenario to explain the origin of the ferroelectric hysteresis is the notion that the domain walls move through a potential generated by their interaction with randomly distributed defects of the matrix. This potential then gives rise to reversible and irreversible domain wall motions resulting in reversible and irreversible changes in the ferroelectric polarization. The exact features of the interaction potential also depend on the stress state of the material which can be influenced by a suitable choice of the substrate. To study the substrate influence, PZT thin films have been deposited on MgO and $SrTiO_3$ single crystals. Electrical characterization methods (hysteresis and small signal capacitance measurements) have been used to extract information on reversible and irreversible polarization contributions.

**11:30 AM F8.11**
APPLICATION OF ULTRAVIOLET RADIATION TO MINIMIZE INTERFACIAL LAYER FORMATION DURING THE GROWTH OF ALTERNATE HIGH-K GATE DIELECTRICS ON Si. J.M. Howard, N.D. Bassim, V. Craciun, R.K. Singh, Univ of Flordia, Gainesville, FL.

One of the major problems associated with the growth of alternate high-k oxide gate dielectrics occurs at the dielectric/Si interface. Namely, there is frequently an additional interfacial $SiO_x$ layer which develops between the two layers. In order to approach ideal thin film dielectric values and electrical properties, it is essential that this layer be minimized. Through the application of ultraviolet (UV) radiation during growth and post-deposition anneals, there has been a marked reduction in this layer. An in depth investigation of the role of oxygen kinetics during the various processing stages for $Y_2O_3$, $ZrO_2$, and $HfO_2$ thin films has been conducted. In this case, the UV radiation is used to break down oxygen into more reactive atomic oxygen species as well as efficiently generate ozone. Both of these oxygen forms have been shown to generate higher quality stoichiometric oxide layers with less physisorbed oxygen. Careful control of oxygen species in conjunction with oxygen barriers built into the deposition process enable the growth of high quility oxide layers with sharp dielectric/Si interfaces. A cadre of characterization including capacitance voltage/current voltage measurements, high resolution STEM-Z images, x-ray photoelectron spectroscopy, and variable angle spectroscopic ellipsometry have been utilized to fully analize the oxide and its interfacial integrity.

**11:45 AM F8.12**
THIN PZT FILM PRESSURE MICROSENSOR. S.I. Khartsev, A.M. Grishin, Dept of Condensed Matter Physics, Royal Institute of Technology, Stockholm, SWEDEN; M.A. Grishin, Dept of Materials Physics, Royal Institute of Technology, Stockholm, SWEDEN.

We report on ferroelectric film pressure sensor fabricated on the top of 4 mm long and 1.2 mm thick Pt80Ir20 tip. PZT film has been deposited by KrF excimer pulsed laser ablation of stoichiometric ceramic target. Since the sensor area is small, about 1.1 $mm^2$, and curved, the optimization of the processing parameters appears to be very critical compared with PZT deposition onto the flat Pt substrates. The following conditions were found to be optimum: substrate temperature is 580°C, energy density is 2-3 $J/cm^2$, and oxygen pressure is 250 mTorr. Sensor fabrication has been completed by depositing small circular, diameter 0.9 mm, Au electrode on the top of PZT film. Dielectric spectroscopy yields dielectric constant of 260 and loss tan delta = 0.034 at 1 kHz, polarization P-E loop tracing shows remnant polarization of 3.8 $uC/cm^2$ while the induced polarization as high as 17 $uC/cm^2$ has been achieved at electric field of 375 kV/cm. Leakage current did not exceed 2 $10^{-6}$ $A/cm^2$ @ 250 kV/cm. To test piezoelectric performance the sensor has been placed in pressure chamber filled with dielectric liquid. The piezo-response has been detected by specially designed low-noise electrometer. It includes electronics performing 400 Hz autozeroing to eliminate random offset drift. Piezoelectric constant as high as 20 pC/N has been measured which is lower than 55 pC/N shown by PZT film deposited at the same conditions onto the bulk flat Pt80Ir20 substrate. This reduction of piezoelectric constant we rely upon the

preferential orientation of PZT film grown on Pt80Ir20 bulk substrate significantly textured during the rolling process. The resolution of thin PZT film pressure microsensor is about 5 mTorr.

SESSION F9: FERROELECTRIC MATERIALS III
Chairs: David P. Norton and David C. Paine
Thursday Afternoon, April 19, 2001
Salon 3/4 (Marriott)

**1:30 PM F9.1**
SELF-ASSEMBLED 3-MERCAPTOPROPYLTRIMETHOXY-SILANE ON $Ba_{0.5}Sr_{0.5}TiO_3$ AS AN ADHESION LAYER FOR MICROWAVE DEVICES. Carlos R. Cabrera[a], Joseph D. Warner, Carl H. Mueller, Fred W. Van Keuls, Félix A. Miranda, NASA-Glenn Research Center, Cleveland, OH; Angel Morales, Rolando Tremont, and Daniel Blasini, Department of Chemistry, University of Puerto Rico at Río Piedras, San Juan, PR; [a]NASA Administrator's Fellow at NASA-Glenn Research Center.

The use of self-assembled monolayers in patterning, in adhesion studies, corrosion protection, sensors, and electronic devices is a growing field. Here we will discuss the use of 3-mercaptopropyltrimethoxysilane (MPS) as an adhesion layer in tunable microwave components using metal/ferroelectric thin film/dielectric heterostructures. In this study, MPS was evaluated as an adhesion layer between a ferroelectric thin film and Au in the development of tunable microwave components. The system studied was the metal/ferroelectric thin film/dielectric heterostructure with the MPS molecule as an adhesion layer between the metal and the ferroelectric thin film. Specifically, we have looked at the interface between the Au layer and $Ba_{0.5}Sr_{0.5}TiO_3$ (BSTO) thin film. It is common to e-beam deposit a chromium adhesion layer, followed by Au, onto BSTO. However, modest diffusion of Cr through the Au will cause an increase of the rf losses of the device. Replacing the chrome interface with a self-assembled structure, such as MPS, can avoid the effect of inter-difussion of chrome in the Au vapor deposited film. In this paper we will present the physical characterization by atomic force microscopy (AFM), ellipsometry, and X-ray photoelectron spectroscopy of the ferroelectric surface modification with MPS and its effect on the vapor deposited Au. In addition, electrical and microstructural data will be correlated.

**1:45 PM F9.2**
RHEED INVESTIGATION OF THE GROWTH OF BARIUM TITANATE ON MAGNESIUM OXIDE. H.Y. Hwang, M. Siegert, Bell Laboratories, Lucent Technologies, Murray Hill, NJ; J. Schubert, Ch. Buchal, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich, GERMANY.

We have studied the growth of $BaTiO_3$ thin films on MgO by pulsed laser deposition by monitoring the growth with a differentially pumped RHEED (reflection high energy electron diffraction) system. The oxygen partial pressure was varied between $5x10^{-6}$ to $5x10^{-2}$ torr, and the growth temperature was varied from 400 to 800°C. Despite the large lattice mismatch of more than 5%, at optimal growth conditions, clear unit cell RHEED oscillations could be observed after the deposition of several 100 nanometers of $BaTiO_3$. We will discuss the correlation between the RHEED oscillation intensity and structural properties as measured by x-ray diffraction, Rutherford backscattering spectrometry and ion channeling.

**2:00 PM F9.3**
SOLUTION DEPOSITION OF BUFFER LAYERS AND MULTI-LAYER YBCO FOR COATED CONDUCTORS. Paul G. Clem, Jeff T. Dawley, Michael P. Siegal, Donald L. Overmyer, Sandia National Laboratories, Albuquerque, NM.

Solution deposition of oriented coated conductors on RABiT and IBAD substrates is a potential method for rapid, low cost production of superconducting tapes. Deposition of YBCO(00l)//$SrTiO_3$(100)//substrate structures has been accomplished on substrates including $LaAlO_3$ (100) and RABiT Ni (200) with Jc (77K) up to 2.4 MA/$cm^2$, and YBCO thickness up to 1.8 um by solution deposition. Strategies for effective integration of buffer layers on Ni, and thick (>1um) multilayering of YBCO will be presented, including understanding of reaction pathway and multilayer pitfalls. Metrics for buffer layer epitaxial quality effects on superconductor Jc and XRD properties will also be discussed. Sandia is a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the US Dept. Of Energy under contract DE-AC04-94A185000.

SESSION F10: OXIDE THIN FILM GROWTH I
Chairs: David P. Norton and David C. Paine
Thursday Afternoon, April 19, 2001
Salon 3/4 (Marriott)

**2:15 PM *F10.1**
HETEROEPITAXIAL GROWTH OF COMPLEX OXIDES ON METALS AND SEMICONDUCTORS. David Norton, Univ of Florida, Dept of MS&E, Gainesville, FL; David Christen, Claudia Cantoni, Hans Christen, John Budai, Matthew Chisholm, Oak Ridge National Laboratory, Oak Ridge, TN.

The formation of crystalline oxides on non-oxide substrate materials involves a complex interplay between the thermodynamic stability and kinetic formation of an ionic/ non-ionic interface. The heteroepitaxial growth of various oxides on both metal and semiconductor surfaces has enabled the integration of functional oxides on useful substrate platforms. Oxide epitaxy on metals is the key component in the RABiTS approach to forming a superconducting tape using the high Tc cuprates. In addition, the use of a crystalline oxide as the gate dielectric in a MOSFET device is currently being pursued by numerous researchers. We will discuss recent results related to epitaxial oxides on metals (Ni, NiCr, Cu) as well as semiconductors (Ge, III-V's). The structural properties of films deposited using pulsed-laser deposition and sputtering will be described. We will also discuss the utility in exploring more complex mulitlayer structures, as this offers the opportunity to create novel oxide materials and device structures, particularly as these efforts extend towards oxide/non-oxide multilayers and superlattices.

**2:45 PM F10.2**
EPITAXIAL GROWTH OF PURE AND DOPED TRANSPARENT CONDUCTING CdO THIN FILMS. Robert P.H. Chang, Min Yan, M.A. Lane, C.R. Kannewurf, Materials Research Center, Northwestern University, Evanston, IL.

Transparent conducting oxides (TCO's) have extensive applications in display devices, solar cells, sensing elements, etc. The ternary alloy system of CdO-$In_2O_3$-$SnO_2$ has received much attention recently. We have initiated a systematic study of the phase diagram by studying the thin film properties of various compounds produced by pulsed laser ablation deposition. In this talk we present results on the epitaxial growth of pure and doped CdO films on MgO(111) substrates. X-ray diffraction pattern of pure CdO film shows a strong and sharp peak at 32.96° [corresponding to CdO (111)] which has a rocking curve of 0.1264°. SEM observation of the film shows that the surface is smooth and without any trace of grains. However, as we increase the amount of doping of either Sn or In, the rocking curve of CdO (111) increases, and the surface of CdO film begins to roughen as observed from SEM. This suggests that the growth mechanism changes from layer by layer growth into island growth. Pure CdO films have conductivities in the range of 1,000S/cm to 4,000S/cm. With the increase of Sn doping, conductivity rises sharply and reaches maximum value of 42,000S/cm at 2.5% of Sn doping. After that point, the conductivity drops quickly. Pure CdO epitaxial film has a bandgap of 2.4eV. The bandgap of CdO film increases with doping and reaches 2.8eV when the dopant percentage is above 6. The Hall effect measurement for the 2.5% Sn doped CdO film has been carried out in the temperature range of 4 - 300K . It is found that carrier concentration is independent of temperature, which suggests that the CdO film is degenerated. Mobility and conductivity increases with the decrease of temperature. The 2.5% Sn doped CdO thin film has a mobility of 580$cm^2$/Vs at room temperature, which is similar to the mobility achieved in CdO single crystal.

**3:30 PM F10.3**
MICROSTRUCTURE AND STRAINS IN THIN FILMS OF $La_2CuO_4$ ON $LaSrAlO_4$-BUFFERED $SrTiO_3$ SUBSTRATES. C.L. Jia, Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Jülich GERMANY; X.H. Zeng, X.X. Xi, Department of Physics, Pennsylvania State University, University Park, PA.

A compressive epitaxial strain in thin films of $La_{2-x}Sr_xCuO_4$ has been found to enhance its superconductivity. The stain can be induced by the lattice mismatch with the substrates when the film thickness is under critical value for misfit relaxation. In the system of $La_2CuO_4/LaSrAlO_4/SrTiO_3$, the thickness of the buffer layer, the interfaces connecting the $La_2CuO_4$ layer and lattice defects are expected to have significant influence on the strain level and strain distribution in the $La_2CuO_4$ layer. In this work, we investigate the microstructure and remaining strain in bilayer films of $La_2CuO_4/LaSrAlO_4$ buffer layers with thicknesses of 37 nm and 75 nm, a compressive strain is measured in the $La_2CuO_4$ layers which have a similar thickness close to the critical value for mismatch-strain relaxation. The strain level in the layer on the 37 nm thick buffer is lower than that in the layer on the 75 nm buffer. The lower level strain can be attributed to an extra relaxation by expansion of the

relatively thin buffer layer. Interfacial stacking faults are found at the interface between the $La_2CuO_4$ and the addition, a strong roughness of the interface is found to induce locally strong lattice bending and extra strain in the $La_2CuO_4$ layer.

**3:45 PM F10.4**
THERMOCHROMIC $VO_2$ FILMS HETEROEPITAXIALLY GROWN ON ZnO COATED GLASS BY RF SPUTTERING. K. Kato, F. Murakami, H. Tatsuhana, Y. Shigesato, Aoyama Gakuin University, Tokyo, JAPAN; H. Odaka, Research Ctr., Asahi Glass Co. Ltd., Yokohama, JAPAN.

Vanadium dioxide ($VO_2$) is one of the most attractive thermochromic materials, which shows large changes in optical and electrical properties at around 68°C, nearly room temperature. This thermochromic behavior has been explained in terms of the Mott-Hubbard transition from a high-temperature rutile structure (metal phase) to a low-temperature monoclinic structure (semiconductor phase). We already reported the r.f. magnetron sputtering using $V_2O_3$ or $V_2O_5$ targets enable us to deposit polycrystalline thermochromic $VO_2$ films with high reproducibility by introduction of oxygen gas ($O_2/Ar+O_2=1\sim1.5\%$) or hydrogen gas ($H_2/Ar+H_2=2.5\sim10\%$), respectively, as reactive gases[1]. However, the thickness of the $VO_2$ films should be larger than 400 nm because stoichiometry x of the $VO_x$ film deposited on glass substrate was higher than 2 (slightly over-oxidation state) in the early stages of the film growth. In this study, ZnO polycrystalline films were deposited as a buffer layer between the $VO_2$ film and glass substrate also by r.f. magnetron sputtering, which have been known to exhibit <001> preferred orientation in the wide range of the deposition conditions. Very thin thermochomic $VO_2$ films with thickness of 70nm were successfully deposited on the ZnO coated glass substrate because of the heteroepitaxial relationship of $VO_2(010)[100]/ZnO(001)[100],[010],[\bar{1}\bar{1}0]$. Such thin $VO_2$ films could be applied for the "smart low-E windows" of the high total energy efficiency in architecture.
1. Y. Shigesato, M. Enomoto and H. Odaka, Jpn. J. Appl. Phys. Vol.39 Part 1, No.10 (2000).

**4:00 PM F10.5**
FABRICATION AND PROPERTIES OF LOW TEMPERATURE SINTERED PZT-PMN FILMS. Eugene Stytsenko and Marc Daglish, Industrial Research Limited, Wellington, NEW ZEALAND.

A film of PZT-PMN composition was fabricated by fine powder deposition from a subsonic airflow on to a tungsten carbide substrate at a temperature of 20°C. The particle flow generated by a jet mill desintegrator circulated inside the cylindrical substrate tube producing a build up on the internal surface of the tube. The film obtained was 70 - 80$\mu$m thick. It was mechanically removed (delaminated) from the substrate and sintered at the temperature of 800°C. The electron microscopy of the green and sintered films showed very dense microstructures with a grain size for the sintered film of 0.2 - 0.8$\mu$m. The permittivity at 1 kHz was about 100 before sintering and 2000 after sintering (unpolarized). The permittivity of the sintered film had the same value as for bulk ceramic samples fabricated from the same powder using conventional isostatic pressing technique and sintered at 1250°C to 97% of the theoretical density. Electric breakdown was observed at 37 kV/mm in the green film and at 10 kV/mm in the sintered film. The saturated hysteresis loop for sintered films was reached at approximately 7 kV/mm. The study showed that the properties of the green body produced by the powder deposition from airflow were superior to the properties of bulk samples prepared by the conventional pressing procedure. The method allowed forming fine microstructures and sintering at the temperature 450°C lower than the normal sintering temperature for the PZT-PMN composition.

**4:15 PM F10.6**
ION-BEAM ASSISTED DEPOSITION OF MgO WITH IN-SITU RHEED MONITORING TO CONTROL BI-AXIAL TEXTURE. James R. Groves, Paul N. Arendt, Stephen R. Foltyn, Quanxi Jia, Raymond F. DePaula, Paul C. Dowden, Harriet Kung, Terry G. Holesinger, Liliana Stan, Luke A. Emmert, and Eric J. Peterson, Matls Sci Div, Los Alamos National Laboratory, Los Alamos, NM.

There is great interest in the high temperature superconductor (HTS) coated conductor community to develop economically scalable processes for fabricating biaxially textured templates on which high-quality $YBa_2Cu_3O_{7-x}$ (YBCO) can be overcoated. To this end, we have studied the growth of magnesium oxide using ion-beam assisted deposition (IBAD) techniques to achieve (100) oriented, biaxially-textured films with low mosaic spread, for film thicknesses of 10 nm. We have refined the process by using reflected high-energy electron diffraction (RHEED) to monitor the growth of IBAD MgO films and found that the intensity versus time curve can be used to control final in-plane texture of the film. Here we present results on our work to develop the IBAD MgO process and the use of real-time RHEED monitoring to deposit well-oriented films. The results have been corroborated with extensive grazing-incidence X-ray diffraction (GID) and dark-field transmission electron microscopy (TEM). Results of these analyses have allowed us to deposit films on metallic substrates with in-plane mosaic spreads less than 7 degrees. The subsequent pulsed laser deposition (PLD) of YBCO HTS superconducting films has resulted in superconducting transport critical current densities >1MA/cm$^2$ (75K, SF).

**4:30 PM F10.7**
STRUCTURAL AND ELECTRICAL CHARACTERISTICS OF $Ba(Zr,Ti)O_3$ THIN FILMS FABRICATED BY ELECTRO-CHEMICAL METHOD AT LOW TEMPERATURE. Chang-Tai Xia, V.M. Fuenzalida, A.R. Zarate, Depto. de Física, U. de Chile, Santiago, CHILE; R.E. Avila, Comisión Chilena de Energía Nuclear, Santiago, CHILE.

Thin films of $Ba(Zr,Ti)O_3$ were fabricated at 60 - 85°C by the electrochemical method from Zr-Ti alloy thin films on the silicon substrates in aqueous solutions of $Ba(OH)_2$. All films were polycrystalline with grain size ranging from nano- to micrometer dimensions. $Ba(Zr,Ti)O_3$ formation was facilitated by increasing the concentration of $Ba(OH)_2$ and the temperature. The film structure was related to the nucleation and growth behavior of the $Ba(Zr,Ti)O_3$ particles. The electrical characteristics were measured in the frequency range from 10 MHz to 10 Hz at room temperature.

**4:45 PM F10.8**
MICROSCOPIC STRUCTURES AT THE INTERFACES OF GALLIUM-GADOLINIUM-OXIDE ON GaAs. T.S. Lay, K.H. Huang, National Sun Yat-Sen Univ, Inst. of Electro-Optical Engineering, Kaohsiung, TAIWAN; W.H. Hung, Synchrotron Radiation Research Center, Hsinchu, TAIWAN; M. Hong, Bell Labs, Lucent Technologies, Murray Hill, NJ.

Electrical experiments have shown that the $Gd_2O_3$, and $Ga_2O_3(Gd_2O_3)$ films are effective passivations to GaAs, while the pure $Ga_2O_3$ does not passivate GaAs [Kwo, J.*etal.*, Appl. Phys. Lett. 75, 1116 (1999)]. In this paper, we have studied the microscopic structures by measuring the depth profile of O 1s, Ga 3d, As 3d, and Gd 4f photoelectron spectra at the interfaces of $Ga_2O_3$, $Gd_2O_3$, and $Ga_2O_3(Gd_2O_3)$ on (100) GaAs substrates. The samples of oxide thickness ~10 nm were grown in a multi-chamber MBE system at a substrate temperature $T_s$ = 550°C. The core level photoelectron spectroscopy was taken with a 90° take off angle at room temperature by using synchrotron radiation beam of photon energies = 120 eV, and 600 eV. The depth profile measurements were performed by choosing $Ar^+$ sputtering at energy $\leq$ 1.5 KeV with an argon partial pressure of $6 \times 10^{-6}$ Torr to minimize preferential sputtering. While no As-oxide components have been observed in the three oxide samples, the depth profile of the photoelectron spectra exhibit very different signatures for Ga 3d and O1s peaks. (1) For the $Ga_2O_3$ sample, the Ga 3d spectra show, in addition to the $Ga_2O_3$ peak, two intermediary oxidation states of binding energies less than $Ga_2O_3$ bonding. The O 1s spectra show one peak at Ga-O bonding. (2) For the $Ga_2O_3(Gd_2O_3)$ sample, the Ga 3d spectra show the $Ga_2O_3$ peak in accompany with a intermediary oxidation state of binding energy ~ 20.3 eV. The O 1s spectra exhibit two peaks, which are related to Ga-O (532.2 eV) and Gd-O (530.1 eV) bondings. (3) For the $Gd_2O_3$ sample, the spectra are very intriguing. While no Ga composition in the oxide layer, a Ga 3d peak is observed at binding energy ~ 20.3 eV as the one shown in $Ga_2O_3(Gd_2O_3)$ spectra. Moreover, two O 1s peaks are detected in the depth profile, one at ~530 eV and the other at ~532eV, also similar to the $Ga_2O_3(Gd_2O_3)$ data. We will discuss the possible interfacial growth revealing from these data.

SESSION F11: OXIDE FILM GROWTH II
Chairs: Stephen K. Streiffer and Hiroshi Katayama-Yoshida
Friday Morning, April 20, 2001
Salon 3/4 (Marriott)

**8:30 AM *F11.1**
COHERENT STRANSKI-KRASTANOW GROWTH OF $YBa_2Cu_3O_{7-\delta}$ on (100) $SrTiO_3$. B. Dam, J.M. Huijbregtse, J.H. Rector, Division of Physics and Astronomy, Vrije Universiteit, Amsterdam, THE NETHERLANDS; B.J. Kooi and J.Th.M. de Hosson, Department of Applied Physics, Materials Science Centre, University of Groningen, Groningen, THE NETHERLANDS.

In hetero-epitaxy both the elastic strain due to lattice mismatch and the substrate-film interaction energy, are the responsible for the SK growth mode. With increasing thickness, the strain energy becomes dominant and at $t_c$ relaxation occurs by the introduction of misfit

dislocations. Recently, it has become clear that heteroepitaxial films are usually also unstable with respect to the formation of coherently strained (dislocation-free) islands which are more or less strain-free near their top and side-walls. This growth mode has been extensively studied in semiconductor heterostructures, where it is the cause for the formation of self-assembled quantum dots (SAQD). The exact nature of this 2D-3D transition is determined by the ratio of strain, surface and interface energies. We studied the the latter type of transition in the first stages of growth of $YBa_2Cu_3O_{7-\delta}$ on (100) $SrTiO_3$ by Pulsed Laser Deposition. Preparing the substrate in either the SrO or $TiO_2$-termination, we isolate the effect of the interfacial energy, leaving both misfit and film surface energy unaffected. We find that (i) pseudomorphic 2D growth occurs up to a critical thickness $t_c = 6.9$ and 19 nm, respectively, while (ii) at $t > t_c$ the films breaks up into *coherent* 3D islands, relieving part of the misfit strain. The dependence of $t_c$ on the termination can only be attributed to the interaction between the substrate terminating plane and the starting atomic layer of the film, which we estimate to be $< 0.39$ J/m$^2$. This is the first time that such a coherent 3D-growth transition is observed in a complex oxide, and on top of that in a tensile epitaxial system. The large rearrangement of the surface indicates the metastable nature of the pseudomorphic growth. Both misfit and threading dislocations form after the growth transition. As the activation energy for dislocation formation is reduced at the island edges, this explains the order observed in the lateral distribution of threading dislocations.

**9:00 AM F11.2**
AUTO FEEDING EPITAXIAL GROWTH OF OXIDE THIN FILM WITHOUT OXIDANT. Kazuo Shimoyama, Kousuke Kubo and Kikuo Yamabe, Inst. of Applied Physics, University of Tsukuba, Ibaraki, JAPAN; Tatsuro Maeda, Electrotechnical Laboratory, Ibaraki, JAPAN.

We demonstrate a high quality epitaxial growth of $BaTiO_3$ thin film on $SrTiO_3$ substrate without oxidant. Epitaxial growth was performed by co-evaporation of Ba and Ti meals by MBE method with shutting off oxygen supply. Although only the metals were supplied to the substrate heated at 973 K in extremely low oxidizing ambient ($pO_2 < 1 \times 10^{-8}$ Pa), a fairly clear RHEED oscillation from layer-by-layer growth of $BaTiO_3$ was observed. The RHEED pattern showed a clear and bright 1×1 streak pattern during and after the growth. The 1×1 streak pattern was maintained as long as the film growth continued to give a thickness of 50 nm. It was found by AES that the film has an approximate stoichiometric composition of $BaTiO_3$. And close investigations of fine structures in Auger peaks revealed that the Ba and Ti atoms in the film were both oxidized to BaO and $TiO_2$, respectively. It was confirmed by XRD that the single-phase oxide $BaTiO_3$ grew epitaxially on $SrTiO_3$ substrate. Oxygen vacancies were found to exist in the $SrTiO_3$ substrate after the growth. Therefore, segregation of lattice oxygen from the bulk substrate into the growing film surface made it possible to oxidize the supplied metals. That is, $BaTiO_3$ grow epitaxially with automatic feeding of oxygen from the oxide substrate. Although considerable amount of oxygen seems to have moved from the substrate to the film through the $BaTiO_3/SrTiO_3$ interface, the interface was abrupt without intermixing. The out of plane lattice constant c of the film deposited without oxidant was determined to be 0.412 nm. This value is larger than that of the film deposited in higher oxygen pressure ($10^{-4}$ Pa). The lattice constant of the film deposited without oxidant remained nearly unchanged after annealing at 873K in 1 atm oxygen pressure for 1 h.

**9:15 AM F11.3**
THIN FILM METAL OXIDE SEMICONDUCTORS DEPOSITED ON POLYMERIC SUBSTRATES. Elvira Fortunato, Patrícia Nunes, Daniel Costa, Donatello Brida, Andreia. Machado, Isabel Ferreira, Rodrigo Martins, FCT-UNL, Caparica, PORTUGAL.

One of the main failure mechanisms of laptop computers, cellular phones, active matrix liquid crystal displays and similar portable devices is the breakage of the glass of the display. To solve this problem much research efforts is focused on the fabrication of thin film electronics on plastic substrates to replace the glass, making these devices flexible, lightweight and unbreakable. In this paper we present results on transparent conducting indium tin oxide (ITO), zinc oxide (ZnO) and tin oxide ($SnO_2$) deposited by spray pyrolysis and rf magnetron sputtering on polyimide substrates with different thicknesses and thermal properties. Although these oxides have been extensively studied on glass substrates, no detail work has been reported on polymeric substrates, especially the mechanical stresses developed in the deposited films. These stresses arise from the thermal expansion mismatch between the substrate and the material. One of the solutions is to re-optimise the deposition process condition of growing them at T<100°C or even at room temperature. The films grown under different substrate temperatures were characterised by: X-ray diffraction; scanning electron microscope, Hall measurements, optical transmittance and atomic force microscope. In order to compare the results, in the experiment performed the same film was also deposited on glass substrate, taken as reference.

**9:30 AM F11.4**
CHARACTERIZATION OF THE INTERFACIAL LAYER FORMED DURING PULSED LASER DEPOSITION OF OXIDES ON Si. V. Craciun, N.D. Bassim, J.M. Howard and R.K. Singh, Univ of Florida, Gainesville, FL.

Future MOS circuits will require new gate materials possessing higher dielectric constants than the currently used $SiO_2$ gate material. The new gate material should form a high quality interface with Si and be able to withstand rather high temperature anneals. It has been reported that after deposition or during the annealing of alternate high-k oxides, an $SiO_x$ layer was formed at the interface between the grown film and the Si. Since this interfacial layer possesses a low-k value, its formation should be prevented or at least minimized. In this letter we present results regarding the growth of the interfacial $SiO_x$ layer during the deposition of thin oxides films such as $Y_2O_3$ and $ZrO_2$ on Si using a pulsed laser deposition (PLD) technique. Although PLD is not a standard technique for microelectronics applications, it is quite suitable for rapid preliminary studies. The optimum oxygen pressure for the growth of $Y_2O_3$ in our system was found to be around 10 mTorr. For this rather high pressure, any deposited layer is bombarded by a huge number of oxygen molecules in any given time interval between two consecutive laser pulses. Some of the oxygen is adsorbed on the surface and then, when the next pulse arrives, gets burried in the film, thus affecting its stoichiometry and microstructure. A clear correlation between the amount of the trapped oxygen inside different oxide layers grown under various conditions and the thickness of the interfacial $SiO_x$ layer was found. Based on these results we suggest that the source for the interfacial layer formation is the oxygen trapped inside the grown layer during the laser ablation process. When the thickness of this low-k $SiO_x$ was reduced by decreasing the oxygen pressure during laser ablation, a marked degradation of the electrical properties of the structures was noticed.

**9:45 AM F11.5**
ELECTRONIC STRUCTURE IN PEROVSKITE TITANATE SUPERLATTICES. Akira Ohtomo, David A. Muller and Harold Y. Hwang, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

In recent years, several mixed-valent transition metal oxides have revealed extensive structure that has been discussed in the framework of charge ordering (examples include $La_{0.5}Ca_{0.5}MnO_3$ and $NaV_2O_5$). We have used laser molecular-beam-epitaxy to grow atomically precise perovskite titanate superlattice films with individual layers as thin as a single unit cell (∼0.4 nm), thereby creating model systems in which we can study local electronic structure. The entire growth process was monitored by RHEED (reflection high energy electron diffraction) observation, demonstrating layer-by-layer growth through the entire superlattice. X-ray diffraction studies of the superlattices demonstrate atomically abrupt interfaces and highly coherent layer stacking. The superlattices could be doped over a wide range of carrier densities, with low temperature Hall mobilities greater than 10,000 cm$^2$/Vs. Using spatially resolved electron energy loss spectroscopy in a scanning transmission electron microscope, we have mapped the electronic structure and cation distribution at the atomic scale, revealing the evolution of the charge states across the superlattice structure.

**10:30 AM *F11.6**
ATOMIC LAYER CONTROL OF EPITAXIAL $SrRuO_3$-$SrTiO_3$-$SrRuO_3$ HETEROSTRUCTURES USING IN-SITU HIGH PRESSURE RHEED FOR SPIN-POLARIZED TUNNEL JUNCTIONS. C.B. Eom, J.H. Choi, J.S. Noh, University of Wisconsin-Madison, Department of Materials Science and Engineering, Madison, WI; G.J.H.M. Rijnders, H. Rogalla, D.H.A. Blank, University of Twente, Department of Applied Physics, Enschede, THE NETHERLANDS; W. Tian, X. Pan, University of Michigan, Department of Materials Science and Engineering, Ann Arbor, MI; J.Z. Sun, IBM T.J. Watson Research Center, Yorktown Heights, NY; B. Oh, LG Electronics Institute of Technology, Seoul, KOREA; H.C. Kim, Korea Basic Science Institute, Taejeon, KOREA.

Atomic scale control of the interfaces in epitaxial complex oxide heterostructures is very important for the fabrication of novel oxide electronic devices. We have grown $SrRuO_3$-$SrTiO_3$-$SrRuO_3$ epitaxial ferromagentic heterostructures on $TiO_2$- terminated (001) $SrTiO_3$ substrates using pulsed laser deposition including $in-situ$ high pressure RHEED. $SrRuO_3$ is an ideal system to study the heteroepitaxial growth mechanism of various perovskite thin films and to fabricate high quality multilayered devices. $SrRuO_3$ is a negatively spin polarized ferromagentic oxide with a lattice parameter of 3.93Å, i.e., a lattice mismatch with (001) $SrTiO_3$ substrates of 0.64%. Our RHEED intensity data and AFM images suggest that the $SrRuO_3$

films on $SrTiO_3$ substrate grow in the step-flow mode with a transition from 2-dimensional layer-by-layer mode into step-flow mode after covering one monolayer of $SrRuO_3$. The origin of the growth mode transition can be attributed to a change in mobility of ad-atoms and switching of a surface termination layer from the substrate into the film. In contrast, the $SrTiO_3$ barrier layer on $SrRuO_3$ bottom electrode grow in the two-dimensional layer-by-layer mode. Transmission electron microscopy images of a cross-sectional $SrRuO_3$-6 unit cell $SrTiO_3$-$SrRuO_3$ heterostructure show that the trilayer is single domain with atomically sharp interfaces between $SrRuO_3$ and $SrTiO_3$. These junctions showed distinct magnetoreistance behavior at low temperature. Quantitative studies of spin-polarized transport across the ferromagnetic oxide (FM-I-FM) trilayer junction interface and the effect of barriers will be discussed.

**11:00 AM F11.7**
ELECTRICAL AND OPTICAL PROPERTIES OF LSCO THIN FILM ELECTRODES PREPARED BY CHEMICAL SOLUTION DEPOSITION. Malin Charoenwongsa, Robert W. Schwartz, Department of Ceramic and Materials Engineering, Clemson University, Clemson, SC.

Lanthanum strontium cobalt oxide (LSCO) has received significant attention for a variety of applications where a conductive oxide material is required. Films of this material have been prepared by a variety of methods including pulsed laser deposition, sputtering, and chemical solution deposition. Despite the broad spectrum of investigations that have been carried out, there are relatively few reports regarding the effects of thickness or grain size on the conduction behavior of this material. Also, reports regarding the influence of substrate type on film properties, or information on the optical properties of these materials in the infrared regions are lacking. In this presentation, we highlight results from our recent investigations of these interrelationships for solution deposited thin films. The grain size of the LSCO 50/50 thin films was observed to vary from 13 to 85 nm with increasing film thickness from 10 to 150 nm. Over this same thickness range, the film resistance was observed to vary from 2000 ohms/sq. to below 90 ohms/sq. Corresponding variations in the resistivity and extinction coefficients were also noted. Compositional factors, such as Sr content, were also observed to affect the grain size, as well as the electrical and optical properties of the films. For films prepared with equivalent thicknesses, a maximum grain size was observed for the LSCO 50/50 composition. As expected, this composition displayed the lowest resistance, but surprisingly, it was also the most transmitting. Finally, we discuss the effects of substrate type, e.g., lanthanum aluminate versus MgO, on the properties of the films. Films prepared on MgO demonstrated significantly poorer conductivity, which was attributed to the greater lattice mismatch of this substrate with LSCO. An investigation of the grain size of the films revealed that the grain size distribution of the LSCO films on MgO was greater than that on lanthanum aluminate.

**11:15 AM F11.8**
GROWTH OF EPITAXIAL HETEROSTRUCTURE $LaVO_3$/$(Pb,La)(Zr,Ti)O_3$/$(La,Sr)CoO_3$. Woong Choi and Tim Sands, University of California, Dept of Materials Science and Engineering, Berkeley, CA.

There has been increasing interest in growing epitaxial perovskite oxide heterostructures for possible novel device structures. One of the interesting structures using the epitaxial heterostructure is the ferroelectric field effect device. In this talk, the growth of perovskite oxide conductor $(La,Sr)CoO_3$, ferroelectrics $(Pb,La)(Zr,Ti)O_3$ (PLZT) and semiconductor $LaVO_3$ in a ferroelectric field effect device configuration will be discussed. The epitaxial heterostructures $LaVO_3$/PLZT/LSCO have been grown on (001) $LaAlO_3$ single crystal substrates by pulsed laser deposition. Structural properties by x-ray diffraction confirmed the epitaxial growth of the heterostructures. Electrical measurements showed that each layer of the heterostructure maintained its bulk properties.

**11:30 AM F11.9**
DIELECTRIC PROPERTIES OF EPITAXIAL $TiO_2$ THIN FILMS. B.H. Park, B.J. Gibbons, J.Y. Huang, D.B. Jan, Q.X. Jia, Superconductivity Technology Center, Los Alamos National Laboratory, Los Alamos, NM; X.Q. Pan, Dept. of Materials Science and Engineering, Univ. of Michigan, Ann Arbor, MI; G. Park, D.G. Deppe, Dept. of Electrical and Computer Engineering, Univ. of Texas as Austin, TX.

$TiO_2$ has applications in microelectronics, solar energy conversion, and photocatalysis. $TiO_2$ mainly exists in two polymorphic phases (anatase and rutile) which show different bulk properties. In this work, we hope to determine whether these differences are manifested in of high quality $TiO_2$ thin films, as well. We have systematically investigated the structural and dielectric properties of both anatase and rutile phase films. Epitaxial $TiO_2$ thin films were deposited on various substrates using pulsed laser deposition. Rutile $TiO_2(110)$, $TiO_2(100)$, and $TiO_2(101)$ films were grown at 650°C on $RuO_2(110)$/$MgO(001)$, $RuO_2(100)$/$LaAlO_3(001)$, and $RuO_2(101)$/R-cut sapphire substrates, respectively. On the other hand, anatase $TiO_2(001)$ and rutile $TiO_2(101)$ were formed at 650°C on $LaAlO_3(001)$ and R-cut sapphire substrates, respectively. Dielectric properties of those films were measured from 100 kHz to 10 MHz. The anatase $TiO_2(001)$ film exhibited comparable dielectric properties with respect to the rutile $TiO_2(101)$ film. This is contrary to the values reported for bulk materials. In this presentation, we will also discuss the microstructures of those epitaxial films analyzed using transmission electron microscopy.