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Final Report

For

Atomic Scale Chemical and Structural Characterization of Ceramic Oxide Heterostructure Interfaces

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DISCLAIMER

1. Project Progress Summary

According to the original proposal, the research plan was divided into three tasks: (a) growth of oxide heterostructures for interface engineering using standard thin film deposition techniques , (b) atomic level characterization of oxide heterostructures using such techniques as STEM-Z combined with AFM/STM and conventional high-resolution microscopy (HRTEM) and (c) property measurements of aspects important to oxide heterostructures using standard charcaterization methods, including dielectric properties and dynamic cathodoluminescence measurements.

Each of these topics were further classified on the basis of type of oxide heterostructure. Type I oxide heterostructures consisted of active dielectric layers, including the materials $Ba_xSr_{1-x}TiO_3$ (BST), Y_2O_3 and ZrO_2. Type II heterostructures consisted of ferroelectric active layers such as lanthanum manganate and Type III heterostructures consist of phosphor oxide active layers such as Eu-doped Y2O3.

Accomplishments in Type I oxides:

- Deposition by *pulsed laser ablation* and optimization of various high and medium-K (dielectric constant) oxide films such as BST, Y_2O_3, and ZrO_2 on Si substrates.
- Characterization of microstructure by atomic scale techniques, including HRTEM, XPS and XRR.
- Characterization and optimization of electrical properties (Capacitance-Voltage and Current Voltage).
- Elimination of thermodynamically stable interfacial SiO_2 layer by high temperature hydrogen ambient anneals to passivate dangling silicon bonds.
- Suppression of interfacial layer formation using silicon surface pre-nitridation prior to deposition of the films
- Nanometer scale chemical characterization of the interface for interfacial layer composition
- Close interaction with Motorola, Inc. and North Carolina A&T University for characterization of electrical properties.

Accomplishments in Type II oxides:

- Deposition by *pulse laser ablation* and optimization of various colossal magnetoresistive films including doped perovskite LMO ($La_{0.7}MnO_{3-\delta}$ doped with Ca, Ba, Sr, Pb) to act as a ferromagnetic biasing source to PBCMO ($Pr_{0.65}Ba_{0.05}Ca_{0.3}MnO_{3-\delta}$) on $LaAlO_3$ substrates.
- Characterization of atomic-scale microstructure by HRTEM, XRD and conventional TEM.
- Characterization of magnetic properties of the oxide films by SQUID
- Deposition and characterization of TMR (Tunneling Magnetoresistance) materials by *pulsed laser ablation* and *sputtering*.
- Enhanced MR ratios and lower transition temperatured of these oxides due to doping refinements in the microstructure.

Accomplishments in Type III oxides:

- Deposition by *pulsed laser ablation* and optimization of europium activated yttrium oxide ($Eu:Y_2O_3$) on various substrates, including quartz, sapphire, Si, and $LaAlO_3$.
- Deposition of diamond buffer layers to enhance surface roughness of the films and consequently the optical properties.
- Characterization of interfaces using STEM-Z microscopy, HRTEM, XRD and XPS.
- Optical property characterization using cathodoluminescence (CL) and photoluminescence (PL).
- Development of a model that predicts the behavior of phosphor thin films based on numerous variables such as substrate type, film thickness, crystallinity, etc.
- Strong interactions with Motorola, Inc. and Oak Ridge National Laboratory in characterization and property measurement.

2. Relevant Papers

Several papers attributable to the work performed and published during the funded period are listed below.

1) K-G Cho, D. Kumar, Z. Chen, P. H. Holloway and R. K. Singh, "Modeling of Cathodoluminescent and Photoluminescent Properties of Pulsed Laser Deposited Eudoped Y2O3 Films," *MRS Symposium Proceedings*, **558**, 21-27 (1999).

2) V. Craciun and R. K. Singh, "In-situ Ultraviolet-assisted Pulsed Laser Deposition of Y2O3 Thin Films," *Electrochemical Solid State Letters, 2: (9) 446-448* (1999).

3) S. L. Jones, D. Kumar, K-G Cho, R. K. Singh and P. H. Holloway, "Pulsed Laser Deposition of Y_2O_3:Eu Thin Film Phosphors," *Displays*, 19, 151-167 (1999)

4) D. Kumar, K-G Cho, Z. Chen, V. Craciun, P. H. Holloway and R. K. Singh, "Cathodoluminescense Properties of Pulsed Laser Deposition Eu-activated Y_2O_3 Epitaxial Films," *Physical Review, B*, 60, 13331 (1999).

5) S. Pietambaram, D. Kumar, R. K. Singh, C. B. Lee and V. S. Kaushik, "Microstructure, Magnetoresistance and Magnetic Properties of Pulsed-laser-deposited External, Internal and Mixed-doped Lanthanum Manganite Films," *Journal of Applied Physics*, 86, 6, 3317-3326 (1999).

6) H. J. Gao, D. Kumar, K-G Cho, P. H. Holloway, R. K. Singh, X. D. Fan, Y. Yan and S. Pennycook, "Epitaxial Growth of Y_2O_3:Eu Thin Films on $LaAlO_3$," *Applied Physics Letters*, **75**, 2223-2225 (1999).

7) V. Craciun, A. Srivastava, J. Howard, R. K. Singh and J. Perriere, "Characteristics of $Ba_{0.5}Sr_{0.5}TiO_3$ Thin Films Grown by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Physics Letters, A*, 69, S787-789 (1999).

8) V. Craciun, J. Howard, E. S. Lambers, R. K. Singh, D. Craciun and J. Perriere, "Low-temperature Growth of Y_2O_3 Thin Films by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Physics Letters, A*, 69, S535-S538 (1999).

9) V. Craciun, J. Perriere, N. Bassim, R. K. Singh, D. Craciun and J. Spear, "Low-temperature Growth of Epitaxial ZnO Films on (001) Sapphire by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Physics Letters, A*, 69, S531-S533 (1999).

10) A. Srivastava, V. Craciun, J. Howard and R. K. Singh, "Enhanced Electrical Properties of $Ba_{0.5}Sr_{0.5}TiO_3$ Thin Films Grown by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Physics Letters*, 75, 3002-3004 (1999).

11) V. Craciun, J. Howard and R. K. Singh, "Ultraviolet-assisted Pulsed Laser Deposition of Thin Oxide Films," *MRS Proceedings*, 574, 193-198 (1999).

12) D. Kumar, K-G Cho, Z. Chen, V. Craciun, P. H. Holloway and R. K. Singh, "Electroluminescent Charastristics of Pulsed Laser Deposited Epitaxial Eu-doped Y2O3 Thin Films," *MRS Proceedings*, 574, 11-17 (1999).

13) V. Craciun, P. Perriere, J. Howard, D. Craciun and R. K. Singh, "Characteristics of ZnO Films Grown by Ultraviolet-assisted Pulsed Laser Deposition," *MRS Fall Meeting*, Boston (1999).

14) V. Craciun, J. Howard, A. Srivastava, R. K. Singh and J. Perriere, "Low Temperature Growth of Barium Strontium Titanate Films by Ultraviolet-assisted Pulsed Laser Deposition," *MRS Fall Meeting*, Boston (1999).

15) K-G Cho, D. Kumar, Z. Chen, P. H. Holloway and R. K. Singh, "Modeling of Cathodoluminescence and Photoluminescence Properties of Pulsed Laser-deposited Europium-activated Yttrium Oxide Thin Film Phosphors," *MRS Proceedings*, 560, 83-87 (1999).

16) S. Pietambaram, D. Kumar, R. K. Singh and C. B. Lee, "Effects of Magnetic and Non-Magnetic Impurity Addition on Magnetoresistance Behavior of Lanthanum Manganite Thin Films," *MRS Proceedings*, 562, 87-91 (1999).

17) D. Singh, R. Houriet, R. Vacassy, H. Hofmann, V. Craciun and R. K. Singh, "Pulsed Laser Deposition and Characterization of $LiMn_2O_4$ Thin Films for Applications in LiIon Rechargeable Battery Systems," *MRS Proceedings, 575, 83-90* (2000).

18) S. Pietambaram, D. Kumar, R. K. Singh, and C. B. Lee, "Electrical, Magnetic and Bolometric Properties of Self-doped and External Doped Lanthanum Manganites," *MRS Proceedings*, 562, 87-92 (2000).

19) V. Craciun, D. Craciun, Z. Chen, J. Hwang and R. K. Singh, "Room Temperature Growth of Indium Tin Oxide Thin Films by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Surface Science*, **168**: No.1-4, 118-122 (2000).

20) V. Craciun, J. Howard, D. Bassim and R. K. Singh, "Low Temperature Growth of High *k* Thin Films by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Surface Science*, **168**: No.1-4, 123-126 (2000).

21) V. Craciun , J. Howard and R. K. Singh, "Enhanced Properties of UV Assisted Deposition of High K Dielectrics," *Proceeding of the 10 Workshop on Physics of Solid State Devices*, Delhi, (2000)

22) V. Craciun, J. Howard, N. Bassim, and R. K. Singh, "Low-temperature Growth of High-*k* Films by Ultraviolet-assisted Pulsed Laser Deposition," *Applied Surface Science*, **168**, 123-126 (2000).

23) V. Craciun and R. K. Singh, "Ultraviolet-assisted Pulsed Laser Deposition of Thin Oxide Films," *Applied Surface Science*, **168**, 239-243 (2000).

24) D. Kumar, J. Sankar, K-G Cho, V. Craciun and R. K. Singh, "Enhancement of Cathodoluminescent and Photoluminescent Properties of Eu:Y_2O_3 Luminescent Films by Vacuum Cooling," *Applied Physics Letters*, **77**, (16), 2518 -2520 (2000).

25) V. Craciun and R. K. Singh, "Characteristics of the Surface Layers of Barium Strontium Titanate Thin Films Deposited by Laser Ablation," *Applied Physics Letters*, **76**, 1932-1934 (2000).

26) V. Craciun, R. K. Singh, J. Perriere, J. Spear and D. Craciun, "Epitaxial ZnO Films Grown on Sapphire (001) by Ultraviolet-assisted Pulsed Laser Deposition," *Journal of Electrochemical Society*, **147**, 1077-1079 (2000).

27) V. Craciun, E. S. Lambers, N. Bassim, R. K. Singh and D. Craciun, "Characteristics of Ultraviolet-assisted Pulsed-Laser-Deposited Y_2O_3 Films," *Journal of Materials Research*, **15**, 488-494 (2000).

28) A. Srivastava, D. Kumar, R. K. Singh, H. Venkataraman and W. R. Eisenstadt, "Improvement in Electrical and Dielectric Behavior of (Ba,Sr)TiO3 Thin Films by Ag Doping," *Physical Review*, **B61** (11) 7305-7307 (2000).

29) H-J Gao, G. Duscher, M. Kim, S. J. Pennycook, D. Kumar, K-G Cho and R. K. Singh, "Cathodoluminescent Properties at Nanometer Resolution Through Z-contrast Scanning Transmission Electron Microscopy," *Applied Physics Letters*, **77**, 594-596, (2000)

30) D. Kumar, S. Chattopadhyay, W. M. Gilmore, C. B. Lee, J. Sankar, A. Kvit, A. K. Sharma, J. Narayan, S. Pietambaram and R. K. Singh, "Structural and Magnetoresistance Properties of $La_{2/3}Ca_{1/3}MnO_3$ Thin Films on Buffered Silicon Substrates," *Applied Physics Letters*, **78** (8), 1098-1100 (2001).

31) S. Pietambaram, D. Kumar, R. K. Singh and C. B. Lee, "Magnetotransport and Magnetic Properties of $La_{0.7}MnO_{3-\delta}$ and $Pr_{0.65}Ba_{0.05}Ca_{0.3}MnO_{3-\delta}$ Superlattices," *Applied Physics Letters*, **78**, 243-245 (2001).

32) D. Singh, R. Houriet, R. Giovannini, H. Hofmann, V. Craciun and R. K. Singh, "Challenges in Making of Thin Films for $Li_xMn_yO_4$ Rechargeable Lithium Batteries for MEMS," *Journal of Power Sources*, **97-98**, 826-831 (2001).

33) D. Singh, V. Craciun, R. Houriet, R. K. Singh, R. Vacassy and H. Hofmann, "Influence of Thin Film Microstructure, Particle Morphology and Crystallinity of Electrochemical Kinetics of LiMnO4 Electrodes for Li Ion Rechargeable Batteries," *Journal Power Sources*, **97-8**, 826-831 (2001).

34) K-G Cho, R. K. Singh, Z. Chen, D. Kumar and P. H. Holloway, "Modeling of Interface Scattering Effects During Light Emission from Thin Films Phosphor for Field Emission Displays," *MRS Proceedings*, **621** (2001).

3. Students Supported Under this Grant

The students currently supported by this grant are:

Nabil Bassim – University of Florida – Ph.D. – 12/2002 grad. date
Joshua Howard – University of Florida – Ph.D. – 12/2002 grad. Date
K.G. Cho – University of Florida – Ph.D. – graduated 5/2000

4. Post Doctoral Researchers supported under this grant

D. Kumar – University of Florida
V. Craciun – University of Florida
H.J. Gao – Oak Ridge National Laboratory