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FY91 End of Fiscal Year Letter
(01 Oct 1991 - 30 Sept 1992)

ONR CONTRACT INFORMATION

Contract Title:	Space charge, heterojunction and elastic stress effects in ferroelectric thin films
Performing Organization:	The Pennsylvania State University
Principal Investigator:	Dr. S.B. Krupanidhi
Contract Number:	#N00014-92-J-1912
R & T Number:	
ONR Scientific Officer:	Dr. Wally Smith

Enclosure (1)

A. DESCRIPTION OF SCIENTIFIC RESEARCH GOALS

(a) Induce low energy ion bombardment related effects in ferroelectric thin films, to enhancing the oxygen incorporation efficiency to modify the properties.

(b) Understanding space-charge related effects on polarization switching phenomena.

(c) Understanding and correlation of intrinsic multi-tunneling process across heterojunctions in ferroelectric thin films.

(d) Establish correlation between low energy oxygen ion bombardment to space-charge and heterojunction based conduction and their impact on polarization switching.

(e) Correlation of switching mechanism via write voltage time dependence to the low energy induced property modifications.

B. SIGNIFICANT RESULTS IN THE PAST YEAR

Role of Low Energy Oxygen Ion Bombardment:

(a) Low energy oxygen ion bombardment has been combined with the growth of ferroelectric PZT thin films using multi-ion beam sputtering method. Significant property enhancement and modification in ferroelectric PZT thin films via low energy oxygen ion bombardment, in terms of increase in dielectric constant, reduction leakage current and increase in the space-charge onset voltage. Films exhibited improved fatigue behavior up to a testing of 10^{11} cycles. No significant loss in retention was noticed in these films up to a duration of 10^6 secs.

(b) Studies were initiated in terms of space charge and switching correlation in ferroelectric PZT thin films. Preliminary results indicated that films which onset a space charge at relatively lower voltages (< 3V), exhibited a lower switching charge density. However, films subjected to low energy oxygen ion bombardment exhibited an improved switching behavior in terms of larger switching charge density in a shorter switching time.

(c) Low energy oxygen ion bombardment during the growth of PZT films also availed a minimized ferroelectric film/substrate interface formations. This gave us an opportunity of depositing high K PZT films on bare silicon substrates. Serious efforts are in progress to gain an understanding of interface parameters.

(d) A low pressure dc glow discharge has been introduced during excimer laser ablation growth of PZT thin films. A specific discharge voltage of 300 V during the ablation appeared to enhance the electrical behavior in every respect. Efforts are in progress to gain a clear understanding of the plasma interaction with the ablation plume. The preliminary understanding makes us believe that the presence of dc glow plasma availed highly reactive

oxygen species thus enhancing the chemistry during the nucleation.

Role of Microstructure on electrical behavior:

(a) The variation in microstructure in ferroelectric thin films often imparts changes in their electrical behavior. This aspect has been studied in detail in La doped $PbTiO_3$ (PLT) thin films deposited by multi-ion beam reactive sputtering. Strict control over the Pb content in the films offers textured PLT films, while the films with slightly excess Pb assumes a regular polycrystalline structure. The most interesting observation is that the textured films exhibited high dielectric constant and high dc resistivity. However, soon after the Pb content exceeds the stoichiometric level, the dielectric constant and dc resistivity dropped significantly. This abrupt behavior has been attributed to the variation in microstructure and its subsequent effect on the electrical behavior. In addition, depending on the state of microstructure, the dc conduction studies revealed a Poole-Frenkle type hopping conduction in the textured films, while the randomly oriented polycrystalline films assumed a space-charge limited bulk conduction in the high voltage regime. Efforts are in progress to obtain a close correlation between the microstructure and the conduction mechanisms in perovskite thin films.

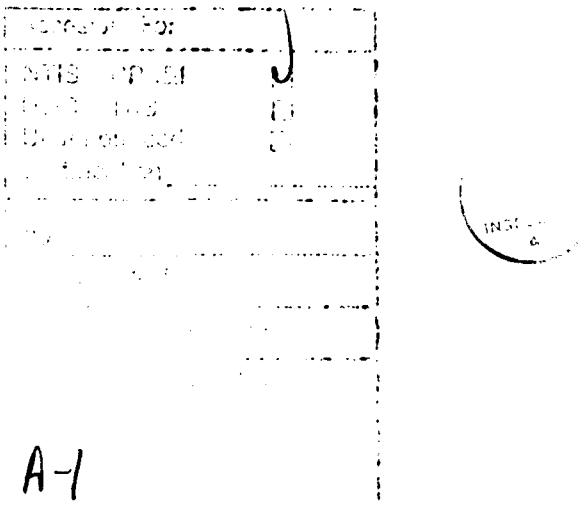
C. PLANS FOR NEXT YEAR'S RESEARCH

(a) Quantify the effective low energy oxygen ion bombardment in terms of dielectric response and conduction behavior.

(b) Detailed studies of space charge related effects on polarization switching time dependence, using both a.c. and d.c. conduction phenomena.

(c) Detailed studies of heterojunction formation at the grain boundaries in ferroelectric PZT thin films at varied oxygen incorporation levels and understanding of their impact on switching phenomena, i.e. ratio of switched charged density and switching time.

(d) Correlation studies of fatigue and retention in ferroelectric PZT thin films with effective oxygen incorporation and modification of grain structure via low energy ion bombardment.



D. LIST OF PUBLICATIONS/REPORTS/PRESENTATIONS

1. **Paper published in refereed journals:**

i) "Pulsed excimer laser ablation and characterization of ferroelectric PZT thin films", D. Roy and **S.B. Krupanidhi**, J. of Materials Research,7,10 (1992).

ii) "Advances in physical vapor growth processes for the growth of device quality ferroelectric thin films", **S.B. Krupanidhi**, J. Vac. Sci. Techn.A, 10, 1569 (1992).

iii) "Excimer laser ablated PZT thin films with low pressure DC glow discharge plasma", **S.B. Krupanidhi** and D. Roy, J. Appl. Phys., (Accepted, 1992).

iv) "Property modification in ferroelectric PZT thin films by low energy oxygen ion bombardment during film growth", H. Hu and **S.B. Krupanidhi**, Appl. Phys., Letters, 61, 1246 (1992).

v) "Composition/Structure/Property relationships in multi-ion beam reactive sputtered (Pb,La)TiO_3 films: Part.I. Composition and structure analysis", G. Fox and **S.B. Krupanidhi**, K.L. More, and L.F. Allarad, J. Materials Research, 7, 11, (1992).

vi) "Evolution of crystallization in rapid thermal processed amorphous ferroelectric PZT thin films", H. Hu, C.J. Peng and **S.B. Krupanidhi**, Thin Solid Films, (Accepted, 1992).

vii) "Switching characteristics of low energy oxygen ion bombardment assisted ferroelectric Pb(Zr,Ti)O_3 films during growth", H. Hu and **S.B. Krupanidhi**, Appl. Phys. Letters, (Accepted, 1992).

2. **Non-refereed publications and published technical reports:**

i). "Pulsed excimer laser ablation and study of multi-component perovskite films for high density DRAM applications", **S.B. Krupanidhi**, D. Roy, C.J. Peng and H. Hu, International Symposium on Integrated Ferroelectrics Proceedings, 1992.

ii) "Impact of low energy ion beam induced effects on the properties of ferroelectric PZT films", **S.B. Krupanidhi** and H. Hu, International Symposium on Integrated Ferroelectrics, Monterey, March 1992, Proceedings.

iii) "Effect of low pressure dc glow discharge in excimer laser ablated PZT films", **S.B. Krupanidhi** and D. Roy, International Symposium on Integrated Ferroelectrics, Monterey, March, 1992, Proceedings.

iv) "Process-property correlation studies in multi-component oxide thin films of ferroelectrics", Indo-US workshop on advanced materials, NPL, Delhi, April, 1992.

v) "Barium Strontium Titanate thin films by multi-ion beam reactive sputtering technique", C.J. Peng, H. Hu, and **S.B. Krupanidhi**, International Symposium on Applications of Ferroelectrics, Sept. 1992, Clemson, SC, Proceedings.

vi) "Controlled ion bombardment induced modification of PZT thin films", H. Hu and **S.B. Krupanidhi**, International Symposium on Applications of Ferroelectrics, Sept. 1992, Proceedings.

vii) "Electrical characterization of multi-ion beam reactive sputter deposited PZT thin films", H. Hu and **S.B. Krupanidhi**, International Symposium on Applications of Ferroelectrics, Sept. 1992, Proceedings.

3. **Presentations:**

a. Invited:

i) "Advances in physical vapor growth processes for the growth of device quality ferroelectric thin films", **S.B. Krupanidhi**, American Vacuum Society Symposium, Seattle, WA, Nov, 1991.

ii) "Impact of low energy ion beam induced effects on the properties of ferroelectric PZT films", **S.B. Krupanidhi**,International Symposium on Integrated Ferroelectrics, Monterey, CA, USA, March 1992.

iii) "Process-property correlation studies in multi-component oxide thin films of ferroelectrics", **S.B. Krupanidhi**, Indo-US workshop on advanced materials, NPL, Delhi, April, 1992.

b. Contributed:

i) "Excimer laser ablated ferroelectric PZT thin films with low pressure glow discharge plasma", D. Roy, **S.B. Krupanidhi** & J.P. Dougherty, American Vacuum Society Symposium, Seattle, WA, Nov, 1991.

ii) "Growth of device quality ferroelectric oxide thin films by excimer laser ablation" **S.B. Krupanidhi**, N. Maffei, D. Roy and C.J. Peng, American Vacuum Society Symposium, Seattle, WA, Nov, 1991.

iii). "Pulsed excimer laser ablation and study of multi-component perovskite films for high density DRAM applications", **S.B. Krupanidhi**, D. Roy, C.J. Peng and H. Hu,

International Symposium on Integrated Ferroelectrics, Monterey, CA, USA, March 1992.

iv) 'Impact of low energy ion beam induced effects on the properties of ferroelectric PZT films", **S.B. Krupanidhi** and H. Hu, International Symposium on Integrated Ferroelectrics, Monterey, CA, USA, March 1992.

v) "Effect of low pressure dc glow discharge in excimer laser ablated PZT films", **S.B. Krupanidhi** and D. Roy, International Symposium on Integrated Ferroelectrics, Monterey, CA, USA, March, 1992.

vi) "Process-property correlation studies in multi-component oxide thin films of ferroelectrics", Indo-US workshop on advanced materials, NPL, Delhi, April, 1992.

vii) "Barium Strontium Titanate thin films by multi-ion beam reactive sputtering technique", C.J. Peng, H. Hu, and **S.B. Krupanidhi**, International Symposium on Applications of Ferroelectrics, Sept. 1992, Clemson, SC.

viii) "Controlled ion bombardment induced modification of PZT thin films", H. Hu and **S.B. Krupanidhi**, International Symposium on Applications of Ferroelectrics, Sept. 1992, Clemson, SC.

ix) "Electrical characterization of multi-ion beam reactive sputter deposited PZT thin films", H. Hu and **S.B. Krupanidhi**, International Symposium on Applications of Ferroelectrics, Sept. 1992, Clemson, SC.

4. **Books (and sections thereof):**

"Multi-ion beam reactive sputtering of multi-component ferroelectric oxide thin films", **S.B. Krupanidhi**, Chapter in Integrated Ferroelectrics, Gordon & Breach Publishers, 1992 (In progress).

E. LIST OF HONORS/AWARDS

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F. PARTICIPANTS AND THEIR STATUS

R. Bill	M.S.,	"ECR plasma effects in ferroelectric thin films for DRAMs"
S.Leiphart	M.S.,	"Multi-magnetron sputter processes in depositing $PbTiO_3$ films"
G. Fox	Ph.D.,	"Microstructure/ process/ property correlation studies in MIBERS grown lead lanthanum titanate thin films"
D. Roy	Ph.D.,	"Excimer laser ablation growth and study of ferroelectric thin films for non-volatile memory devices"

H. Hu Ph.D., (In progress)
N. Maffei Ph.D., (In progress)
J. Belsick Ph.D., (In progress)

G. OTHER SPONSORED RESEARCH DURING THE YEAR FY91

i) Development of device quality ferroelectric thin films for memory applications, DARPA/ONR, $250,000/year, July 1989-November 1992.

ii) Development of low temperature growth process for hysteretic ferroelectric thin films, McDonnel Douglas, $100,000/year, Jan 1991-Dec 1991.

iii) Ferroelectric thin films for microcapacitor applications, Ben Franklin, $90,000/year, Aug 1989-Dec 1991.

H. SUMMARY OF FY92
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/PARTICIPANTS
(Number Only)

		ONR	non ONR
a.	Number of Papers Submitted to Referred Journal but not yet published:	6	5
b.	Number of Papers Published in Refereed Journals:	7	6
c.	Number of Books or Chapters Submitted but not yet Published:	1	2
d.	Number of Books or Chapters Published:	—	—
e.	Number of Printed Technical Reports & Non-Referred Papers:	7	3
f.	Number of Patents Filed:	—	—
g.	Number of Patents Granted:	—	—
h.	Number of Invited Presentations at Workshops or Prof. Society Meetings:	3	3
i.	Number of Contributed Presentations at Workshops or Prof. Society Meetings:	9	4
j.	Honors/Awards/Prizes for Contract/Grant Employees: (selected list attached)	—	—
k.	Number of Graduate Students and Post-Docs Supported at least 25% this year on contract grant:	6	4
	Grad Students: TOTAL	6	4
	Female	—	2
	Minority	2	—
	Post Doc: TOTAL	—	—
	Female	—	—
	Minority	—	—
l.	Number of Female or Minority PIs or CO-PIs	—	—
	New Female	—	—
	Continuing Female	—	—
	New Minority	—	
	Continuing Minority	—	

Enclosure (

ONR FOREIGN TRAVEL POLICY