Revised Final Report

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"Oxide Ferromagnetic Semiconductors for Spin-Electronic Transport"

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Introduction

The *objective* of this research project was to investigate the viability of oxide magnetic semiconductors as potential materials for spintronics. We identified two members of the solid solution series of ilmenite and hematite for our investigation based on their ferromagnetic and semiconducting properties. For the sake of simplicity we call in general this solid solution series as IH. It consists of many members in whom the ratio between ilmenite ($FeTiO_3$) and hematite (Fe_2O_3) can be varied between 0 and 0.67. Above this value of x IH does not form solid solution. Its general formula is $(1-x)FeTiO_3.xFe_2O_3$. The nature of semiconductor of this series changes from p-type semiconductor to n-type semiconductor for x= 0.18. Below this concentration IH is p-type; and above it n-type. Similarly, as the concentration of hematite increases so does the magnetic Curie point and the electrical conductivity. Our previous research led us to believe that IH with 33 (IH33) and 45 atomic percent hematite (IH45) were potential candidates for our search for suitable materials for spintronics. Both are wide bandgap semiconductors with the magnetic Curie point well above the room temperature. During the course of our studies for their magnetic and semiconducting properties we realized that room temperature magnetic semiconductors were not limited only to the members of the IH series. By carefully modifying the basic Fe-titanates we identified other suitable materials for our studies. We expanded the scope of our investigation in search of suitable oxides for spintronics and included Mn-substituted ilmenite ($FeTIO_3$) and Mn-substituted pseudobrookite (Fe_2TIO_5). We produced, for the first time, both these materials with magnetic Curie points above room temperature, well defined magnetic hysteresis loops, and electrical conductivity comparable to those of IH33 and IH45. These discoveries have been reported in publications #s 1, 2 and 14.

In order to meet our *objective* we set the following goals for us to pursue:

- Growth and characterization of epitaxial films by pulsed laser deposition (PLD) on suitable single crystal substrates such as sapphire (Al_2O_3) and magnesium oxide (MgO);
- Characterization for determining structural (by XRD, SEM and TEM methods), electrical and magnetic properties;
- Determination of the values and nature of their band gaps by photoluminescence studies;
- Theoretical studies leading to modeling of electronic structures to explain the conduction mechanism and associated semiconductor properties;
- Determination of radiation hardness of these materials to investigate their usefulness in fabricating devices for radhard electronics;
- Fabrication and performance evaluation of a junction device (such as a diode or a transistor) or a tunneling device;
- Determination of spin mediated coupling properties.

We met almost all these goals except: 1. the theoretical studies leading to modeling of electronic structures to explain the conduction mechanism and associated properties because of lack of sufficient supporting data and complexity of the nature of the IH and 2. Fabrication and performance evaluation of a junction device because of the difficulties in processing a junction suitable for the transport of current. Instead we produced some novel devices such as varistors and three-terminal devices that can be used for producing bipolar currents. These devices show excellent radiation resistance when irradiated with neutrons, protons and heavy Fe-ions.

It is to be appreciated that we not only met most of our goals rather expanded vastly the scope of research by including investigations of Mn-$FeTiO_3$, Mn-Fe_2TiO_5 and by producing a novel three terminal device capable of generating bipolar currents.

Sample Preparation and Results

Three types of samples were processed in our labs for these studies: dense and homogenous ceramic (polycrystalline), films both epitaxial and textured, and bulk single crystals of Fe_2TiO_5. We could not produce bulk single crystal of IH because of the dissociation problems at high temperatures. Single crystals of Mn-$FeTiO_3$ were not tried for lack of time and instrumentation. First the ceramic samples were studied for their structural, magnetic and electronic properties. They were then processed by careful optimization to produce samples with the best physical properties. They were also used as targets for the growth of films by the PLD method. Epitaxial films were grown on sapphire substrates and evaluated for the magnetic and semiconducting properties. The growth parameters and physical properties of these films are reported in papers #s 3 and 4.

The results of their structural and physical properties have been extensively reported in publications #s 1through14. Effect of irradiation by protons, neutrons and Fe-ions on electronic, magnetic and device performance are reported in publications # 1, 7,8,10, and 14. An integrated magnetic switching device consisting of IH 33 epitaxial film and nickel film was produced, evaluated and reported in publication # 12. They were also used for the fabrication of the three terminal electronic device which was then reported also in the publication # 12. Textured films were grown on MgO substrates, evaluated for the physical properties and then used for fabrication of radiation hardened varistors and reported in our multiple publications as described earlier in this report.

Summary

During the course of this project we limited our efforts in studying four modified members of the Fe-titanates series. Their selection was based on their desirable magnetic and electronic properties. They were: IH33 (ilmenite-hematite with 33 atomic percent hematite), IH45 (ilmenite-hematite with 45 atomic percent hematite), Mn-substituted ilmenite (Mn-$FeTiO_3$), and Mn-substituted pseudobrookite (Mn-Fe_2TiO_5). All of them are wide bandgap semiconductors with band gaps ranging in values between 2.5 to 3.5 eV, n-type semiconductor, all of them exhibit well defined magnetic hysteresis loops and magnetic Curie points greater than 400K. Ceramic, film and single crystal samples were studied and based on their properties we produced varistors (also known as voltage dependent resistors) for IC circuit protection from power surges, a three-terminal current-voltage device capable of generating bipolar currents, and a novel spin value capable of controlled magnetic switching of spins. Eleven refereed journal papers, three refereed conference papers and three invention disclosures resulted from our investigations. We also presented three invited papers in two international conferences and one national conference. Furthermore two students graduated with Ph.D. degrees, three with M.S. degrees and one with B.S. degree. In all our publications, conference and seminar presentations, dissertations and theses sponsorship of DOE has been acknowledged. Also two post-doctoral fellows were actively involved in this research. We established the radiation hardness of our devices in collaboration with a colleague in a HBCU institution, at the Cyclotron Center at Texas A&M University, and at DOE National Labs (Los Alamos and Brookhaven). We are particularly happy not only to meet most of our research goals rather also to discover two new room temperature magnetic semiconductors, namely, Mn-$FeTiO_3$, Mn-Fe_2TiO_5 and by producing a novel three terminal device capable of generating bipolar currents. Furthermore we conclusively established the radiation hardness of these four modified iron titanates.

Publications: Refereed Journal Paper; Refereed Conference Papers and Invention Disclosures

Refereed Journal Papers

1. R. K. Pandey, P. Padmini, R. Schad, J. Dou, H. Stern, R. Wilkins, R. Dwivedi, W. J. Geerts, and C. O'Brien, " Novel magnetic-semiconductors in modified iron titanates for radhard electronics" J. Electroceramics, DOI 10.1007/s10832-007-9390-1, (2008).

2. P. Kale, P. Padmini, J. Dou, L. Navarette, R. Schad and R.K. Pandey, "First evidence of Ferromagnetism in Mn substituted $FeTiO_3$ ceramics" J. Am Cer. Soc (in press).

3. J. Dou, L. Navarette, R. Schad, P. Padmini, R. K. Pandey, H. Guo and A. Gupta, "Magnetic properties of ilmenite-hematite films and bulk samples", *J. Appl. Phys*, 103, (2008), 07D117.

4. J. Dou, L. Navarette, P. Kale, P. Padmini, R.K. Pandey, H. Guo, A. Gupta and R. Schad, "Properties of Epitaxial Ilmenite-Hematite Films as a Function of Oxygen Content", J. Appl. Phys., 101, (2007),053908.

5. P. Kale, P. Padmini, J. Dou, L. Navarette, M. Shamsuzhoa, R. Schad and R.K. Pandey, " Growth and Characterization of Ilmenite-Hematite thin films by Pulsed Laser Deposition" J. Electronic Mats,9, (2007),1224.

6. L. Navarrete, J. Dou, D.M. Allen, R. Schad, P. Padmini, P. Kale and R.K. Pandey, "Magnetization and Curie point of Ilmenite-Hematite solid solution ceramics." J. Amer. Ceram. Soc., 89(5), (2006), 1601.

7. P. Padmini, S. Ardalan, F. Tompkins, P. Kale, R. Wilkins and R. K. Pandey, "Influence of proton radiation on the current-voltage characteristics of ilmenite-hematite ceramics", *J. Elec. Mats,34(2), 1095 (2005)*.

8. D. M. Allen, L. Navarrete, J. Dou, R. Schad, P. Padmini, P. Kale and R. K. Pandey, S. Shojah-Ardalan and R. Wilkins, " Chemical ordering in ilmenite-hematite bulk ceramics through proton irradiation", *Appl. Phys. Lett.* 85, (2004), 5902.

9. Amrit Bandyopadhyay, Julian Velev, W.H. Butler, Sanjoy K. Sarker, and O. Bengone, "Effect of Electron Correlations on the electronic and magnetic struceture in Ti-doped a-hematite", *Physical ReviewB*, 69, (2004), 174429-1.
10. P. Padmini, M. Pulikkathara, R. Wilkins and R. K. Pandey, " Neutron radiation effects on the nonlinear current-voltage characteristics of ilmenite-hematite ceramics," *Appl.Phys.Lett.*, 82(4), (2003), 586.

11. W.H. Butler, A. Bandyopadhyay, and R. Srinivasan, "Electronic and Magnetic Structure of a 1000 K Magnetic Semiconductor: a-hematite (Ti)", *J. Appl. Physics*, 93, (2003), 10.

Refereed Conference Papers

12. R. K. Pandey, H. Stern, W. J. Geerts, P. Padmini, P.Kale, J. Dou, and R. Schad, " Room Temperature Magnetic-Semicondctors in Modified Iron Titanates: Their Properties and Potential Microelectronic Devices", Advances in Science and Technology, 54, (2008), 216.

13. Christopher Lohn, Wilhelmus J. Geets, Chris S. O'Brien, J. Dou, P. Padmini, R. K. Pandey, and R. Schad, " IV and CV Characteristics of Multifunctional Ilmenite-Hematite 0.6 FeTiO3.0.333 Fe2O3.", in book entitled "Functional Nanoscale Materials, Devices and Systems edited by A. Vaseashta and I. N. Mihaliescu Scie:, NATO nce for Peace and Security Series B: Physics and Biophysics, ISSN 1874-6500, Published by Springer Netherlands, (2008), 419.

14. R.K. Pandey, P. Padmini, L.F. Deravi, N.N. Patil, P. Kale, J. Zhong, J.Dou, L. Navarette, R. Schad and M. Shamzuzhoa, "Magnetic Semiconductors in Fe-Ti_Oxide Series and their Potential Applications", IEEE Proceedings of the 8th International Conference on Solid State and Integrated Circuit Technology, ICSICT 2006, Part 2, 2006, 992-997, ISBN: 1-4244-0160-5, (2006), 992.

Invention Disclosures

The following three invention disclosures originating from this research were filed to the Office of Technology Transfer of the University of Alabama. But their decision was not to file patent applications because it was assumed that these inventions may not have commercial values.

15. UAIPD 07-003: "Magnetic Field Tunable Varistors", Inventors: Padmini Periaswamy, R. K. Pandey, Jian Dou and Rainer Schad.

16. UAIPD 07-013: "A Novel Multilayered Device for Controlled Magnetic Switching", Inventors: Rainer Schad, Jian Dou, Padmini Periaswamy and R. K. Pandey.
17. UAIPD 07-016: "A Novel Microelectronic Device", Inventors: R.K. Pandey, Padmini Periaswamy, Harold Stern, Jian Dou and Rainer Schad. (Provisional Patent Application Filed, August 2007; not converted to Full Patent Application).

Students Educated

Ph.D. graduated: D.M. Allen and Jian Dou, both in Physics.

M.S. graduated: L. Navarrete (Physics), P. Kale (Electrical Engineering), and N. N. Patil (Computer Science).

B.S. graduated: Leila F. Deravi (Chemistry).

All were students are the University of Alabama at Tuscaloosa, AL

Postdoc Trained

Dr. P. Padmini and Dr. Julian Velev.

Collaboration

(a) DOE National Labs

- LANL, Brookhaven National Lab
- Cyclotron Radiation Center at Texas A&M University, College Station, TX for Proton radiation of samples

(b) Universities

- Rick Wilkins, an Associate Professor of Electrical Engineering at Prairie View A&M University, Prairie View, TX, which is a HBCU institution. Dr. Wilkins was instrumental in getting our samples radiated at the DOE National Labs., and at Texas A&M University. This effort led to 4 (# 1, 6, 7 and 8) publications. Also 2-3 graduate and undergraduate African-American and female students got some education in studying the effect of radiation on the electrical properties of our samples. Two of these students are co-authors in our publications (# 7 and 10)
- Dr. Wim Geerts, an Associate Professor of Physics at Texas State University, San Marcos, TX. Here he and his graduate students helped us doing Hall Effect, Magneto resistance and 3-terminal I-V measurements. This collaboration led to

three publications. Two of his graduate students used some of our samples to do their own M.S. Thesis research. Both are co-authors in our publications (# 1,13 and 14).