PULSED LASER DEPOSITION - A REVIEW

Richard Pinto
Department of Electrical Engineering
Indian Institute of Technology Bombay
Powai, Mumbai 400076
Email: rpinto@ee.iitb.ac.in

Abstract

Although pulsed laser deposition (PLD) had its origin in the early 1980's,it came into prominence in 1987 with the first realization of thin films of high Tc superconductor YBa2Cu3O3-x (YBCO) using this growth technique. In the absence of a convenient technique for the growth of high quality films of multicomponent oxide materials, PLD has advanced phenomenally during the last 18 years - first with the realization of thin films of high Tc superconductors, and subsequently of colossal magnetoresistance (CMR) and ferroelectric materials. Further, the ability to realize high quality films from small targets (unlike the requirement of big targets in sputtering) has made the PLD technique extremely attractive for research laboratories. However, two disadvantages viz, particulate formation and the difficulty in realizing films on large area substrates, have made PLD virtually limited to research laboratories.

In this talk I shall discuss the physics and the kinetics of thin film growth by PLD and its progress since it was first used for YBCO film growth in 1987. From growth kinetics considerations, PLD is perhaps the most complex of the techniques, and yet, as experience has shown, it is the most convenient and versatile among the techniques for the realization of multicomponent oxide thin films. This talk will review the impact of the PLD technique in the light of our own work (carried out at TIFR since 1991) in the realization of high quality films of high Tc superconductors, CMR materials, ferroelectrics and multiferroics. I shall also highlight the contributions of PLD in the realization of some of our finest results such as highest Jc YBCO films, first synthesis of unstable LuBa2Cu3O7-x thin films, synthesis of ferroelectric PbTiO3 films on <100> Si, and the recent work on multiferroic BiFeO3 films and Bi0.6Dy0.3La0.1FeO3 films which show coexistence of ferroelectric and magnetic ordering.

Pulsed Laser Deposition for MOS Gate Dielectric Films

Nandita DasGupta*, RavneetSingh, Roy Paily, Amitava DasGupta, Pankaj Misra and Lalit M. Kukreja

** Department of Electrical Engg., IIT Madras, Chennai 600 036*

*Email: nand@ee.iitm.ernet.in

Abstract

Downscaling of device dimensions is essential for the development of new generation Ultra Large Scale Integrated Circuits (ULSI) based on Complementary Metal Oxide Semiconductor Field Effect Transistors (CMOSFET). Silicon dioxide(SiO_2) has been used for more than 35 years as the primary gate-dielectric material in MOSFETs because of its excellent properties. However, current technology requires that the thickness of the gate dielectric be reduced to only a few monolayers of SiO_2. Further thinning of SiO_2 poses a serious challenge because of large gate leakage current[1,2]. In order to overcome the large gate leakage current mainly due to direct tunneling, introduction of new gate dielectric materials with high dielectric constant (high-k) is being seriously investigated [3-6]. Using high-k dielectric, the physical thickness of the dielectric layer can be kept large, thereby reducing the gate leakage current, while maintaining the same value of capacitance. There are many materials systems under consideration which have potential to replace SiO_2 as the gate dielectric material. Of the various high-k dielectric materials, TiO_2, Ta_2O_5, ZrO_2, and HfO_2 have generated a lot of interest due to their high dielectric constant and adequate barrier height. Various deposition techniques have been employed to deposit these materials.

We have recently reported for the first time, the use of Pulsed Laser Deposition (PLD) technique for the deposition of TiO_2 as gate dielectric in Metal-TiO_2-SiO_2-Si (MTOS) capacitors with TiO_2-SiO_2 stacked gate dielectric[7, 8]. One interesting observation in our work is that by optimizing the conditions during PLD, one can actually achieve an increase in capacitance of the MTOS capacitor by introducing the additional TiO_2 layer over SiO_2. The reduction in the Effective Dielectric Thickness (EDT), defined as $\varepsilon_{ox}A/C_{max}$, where ε_{ox} is the dielectric constant of SiO_2, A is the device area and C_{max} is the accumulation capacitance is due to an intermixing of the TiO_2 layer with the underlying SiO_2.

Previous reports indicate that it has been rarely possible to obtain an EDT < 2 nm using TiO_2 thin films [3]. We have however, been able to combine the reduction in the EDT with a reduction in the gate leakage current by controlling the intermixing of the TiO_2 and SiO_2 layers during PLD. To achieve this, we have used a dual-temperature deposition process, where a buffer layer of TiO_2 has been deposited at low temperature followed by deposition of TiO_2 at higher temperature and annealing resulting in an EDT < 2 nm as well as low leakage [9]. As shown in Fig.1, the leakage current densities (J) of the MTOS devices are at least five orders of magnitude smaller than that in the simulated MOS devices with comparable EDT. It can also be seen that while for the simulated MOS devices, the leakage current changes by five orders of magnitude as the gate oxide thickness reduces from 2.5 to 1.5 nm, for the MTOS devices, the leakage current changes only by one order of magnitude for a similar reduction in EDT from 2.4nm to 1.6 nm. This is because, the leakage current is determined by the physical thickness and the

physical thickness of the gate dielectric for these MTOS devices is comparable, even though their EDT values are different.

Even though the results of MTOS devices have been encouraging, for preserving the interface quality, a very thin layer of SiO_2 has to be grown on silicon prior to PLD of TiO_2. Conventional thermal oxidation has been used for growing this thin SiO_2 layer. It would, however, be extremely useful if both PLD of TiO_2 and the growth of SiO_2 can be carried out using the same process. To this end, we have developed a novel technique of Laser Induced Oxidation (LIO) to grow ultrthin SiO_2 (<4nm) using only a pulsed laser source and maintaining the substrate at room temperature [10]. Pulsed laser source generates energy pulses of nano-seconds time duration. These short time pulses have been used to heat the silicon wafer surface in O_2 ambient to grow SiO_2 in a very controlled manner. As shown in fig.2, the leakage current density was found to be low and the breakdown field strength high (> 10 MV/cm for LIO3), signifying the excellent quality of the Laser-induced oxide.

References

1) S. -H. Lo, D. A. Buchanan, Y. Taur, and W. Wang, IEEE ED Lett. 18 (1997) 209.
2) D.A.Buchanan and S.H.Lo, Microelectronic Engineering 36 (1997) 13.
3) Masaru Kadoshima, Masahiko Hiratani, Yasuhiro Shimamoto, Hiroshi Miki, Shinichiro Kimura, Toshihide Nabatame, Thin Solid Films, 424 (2003) 224.
4) Jing-Chi Yu, B.C. Lai, J.Y. Lee, IEEE ED Lett. 21 (2000) 537.
5) W. K. Chim, T. H. Ng, B. H. Koh, W. K. Choi, J. X. Zheng, C. H. Tung, A.Y. Du, J. Appl. Phys. 93 (2003) 4788.
6) Q. Fang, J.-Y. Zhang, Z. M. Wang , J. X. Wu, B. J. O'Sullivan, P. K. Hurley, T. L. Leedham, H. Davies, M. A. Audier, C. Jimenez, J.-P. Senateur, Ion W. Boyed, Thin Solid Films, 428 (2003) 263.
7) Roy Paily, Amitava Das Gupta, Nandita Das Gupta, Pijush Bhattacharya, Pankaj Mishra, Tapas Ganguli,Lalit M. Kukreja, A.K. Balamurugan, S.Rajgopalan, A.K.Tyagi, Applied Surface Science 187 (2002) 297.
8) Roy Paily, Amitava DasGupta, Nandita DasGupta, Pankaj Misra and Lalit M.Kukreja, Thin Solid Films, Vol. 462-463C pp. 57-62, 2004.
9) Ravneet Singh, Roy Paily, Amitava DasGupta, Nandita DasGupta, Pankaj Misra and Lalit M. Kukreja, Semiconductor Sc. & Technol., Vol.20, No.1, Jan.2005
10) Ravneet Singh, Roy Paily, Amitava DasGupta, Nandita DasGupta, Pankaj Misra and Lalit M. Kukreja, Electronics Letters, Vol. 40, No.25, pp.1606-08, Dec. 9, 2004

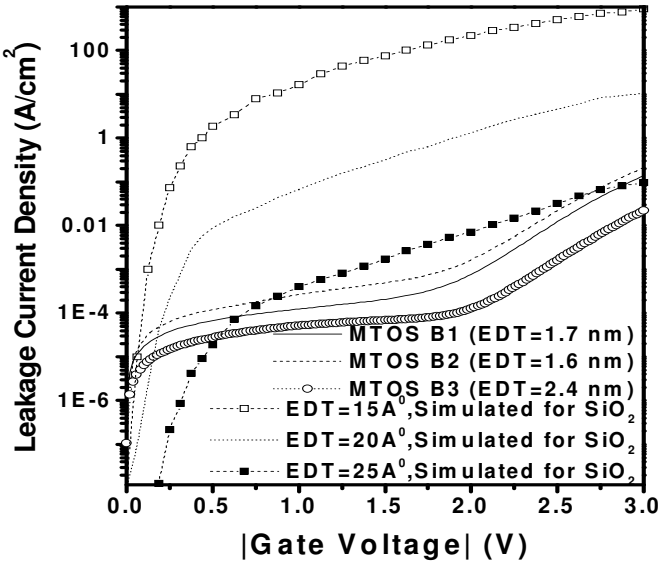


Fig.1: Comparison of J-V characteristics of MTOS devices with those of simulated MOS devices with comparable EDT

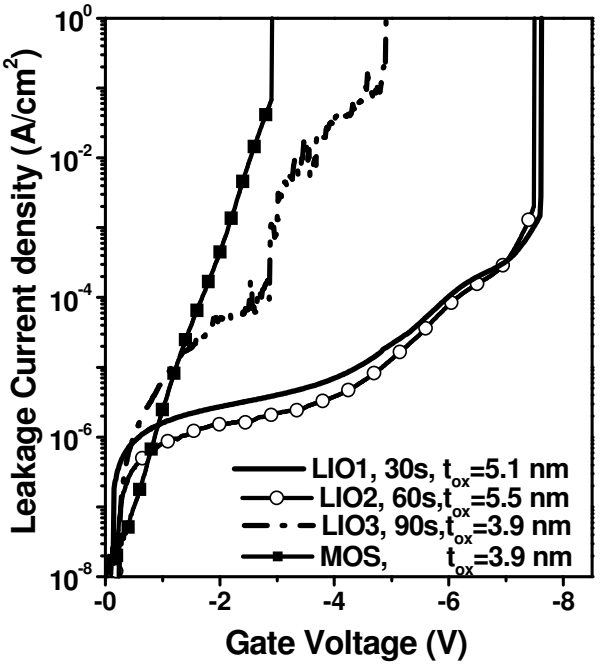


Fig. 2. J-V characteristics of LIO1, LIO2, LIO3 and MOS capacitors.

Some studies on oxide and nitride thin films grown by pulsed laser deposition

K. P. Adhi

Centre for Advanced Studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune - 411 007, India

Email: kpa@physics.unipune.ernet.in

Abstract

Pulsed laser deposition (PLD) has emerged as a relatively simple and highly versatile technique for the growth of thin films of variety of materials[1]. Deposition of epitaxial, stoichiometric thin films of simple materials[2] or multi-element complex compounds on suitable substrates[3], multilayers[4], nano-particles[5] and nano-structures etc. are some of the achievements which reflect the versatility of this technique. We present a review of our recent research work on the growth, characterization and analysis of oxide and nitride thin films. The presentation is focused on the following oxide materials; a) Fe_3O_4 b) $La_{0.7}Ca_{0.3}MnO_3$ and c) bi-layers of Fe_3O_4 / $La_{0.7}Ca_{0.3}MnO_3$. Some of the issues which will be addressed are growth of highly oriented thin films of the above mentioned materials, modifications in their structural and electrical properties due to external processing like swift heavy ion irradiation, ionimplantation etc . In case of nitrides, the growth of highly oriented AlN thin films on sapphire, its characterization along with brief mention of InN and GaN thin films will be discussed. Generation of nanoparticles of Fe_3O_4 / FeO by PLD will also be discussed.

References:

1. "Pulsed Laser Deposition of Thin Films" edited by D. B. Chrisey and G. K. Hubler, A Wiley – interscience publication, New York (1994)
2. S. M. Jejurikar, A. G. Banpurkar, A. V. Limaye, S. K. Date, S.I. Patil, K. P. Adhi, P. Misra, L. M. Kukreja, Ravi Bathe, communicated to J. Appl. Phys.
3. Ravi Bathe, K. P. Adhi, S. I. Patil, G. Marest, B. Hannoyer, S. B. Ogale, Appl. Phys. Lett. **76**, 2104 (2000)
4. S. N. Sadakale, R. J. Choudhary, M. S. Sahasrabudhe, A. G. Banpurkar, K. P. Adhi, S. I. Patil, S. K. Date, J. Mag. Mag. Mater. 286, 450 (2005)
5. S. R. Shinde, A. G. Banpurkar, K. P. Adhi, A. V. Limaye, S. B. Ogale, S. K. Date, G. Marest, Mod. Phys. Lett. B **10**, 1517 (1996)

Micro- nano patterning in a single step via selective laser ablation

Alika Khare
Department of Physics
Indian Institute of Technology Guwahati, Guwahati 781039
Email: alika@iitg.ernet.in

Abstract:

Optoelectronics devices viz; grating couplers, micro mirrors, tiny arrays of lasers and photonic band gap materials require ordered arrays of dimensions ranging from nanometers to tens of microns. These tiny arrays of materials can be produced by modifying the surface morphology of thin films by illuminating it with interference pattern formed by interference of multiple beams from a pulsed high power laser. The interference patterns are periodic, so the materials of the thin film exposed to the maximum intensity (bright fringe) gets ablated leaving the area of minimum intensity (dark fringe) unaffected. Width and periodicity of the ablated region depends on the intensity distribution with in the bright fringe and wavelength of laser respectively. For writing the grating like structure, a simple two beam Michelson interferometer can be used. For patterning in the format of arrays of dots of the material in square or rectangular geometry, two Michelson interferometers in tandem can be used. For hexagonal geometry, interference pattern from the eight beams coming out of system of three interferometers in tandem can be used. This is a direct lithographic technique without requiring any mask. The whole writing can be performed in a single step. The technique of selective laser ablation via high power interferometer can be applied to the thin film of any material. The material ablated from the region of bright fringe results into the formation of arrays of cold atomic beam having relatively low divergence. The application of these atomic beams for nano lithography via dipole force shall also be presented in the talk.

Electron doped rare-earth manganites: A current scenario

Pratap Raychaudhuri

Department of Condensed Matter Physics and Materials Science,Tata Institute of Fundamental Research,

Homi Bhabha Rd., Colaba, Mumbai-400005.

Email: pratap@tifr.res.in

Abstract

Electron doped rare-earth manganites of the form ($R_{1-x}A_xMnO_3$, where R=rare-earth, A=tetravalent cation) fall the class of compounds which have so far been synthesized in single phase only through the pulsed laser deposition technique. The most well known member of this series $La_{1-x}Ce_xMnO_3$ was first synthesized in TIFR in 1999 and showed the magnetic and transport properties to be very similar to its hole-doped counterpart [1]. Subsequently, studies using a variety of techniques such X-ray absorption spectroscopy[2], Tunneling conductance in artificial tunnel junctions with $La_{0.7}Ce_{0.3}MnO_3$[3] established this material to be a minority spin carrier ferromagnet where the manganese is in a mixture of Mn^{3+} and Mn^{2+} valence states. These findings led to an active search for other electron doped manganites among many groups in recent years and several new candidates have been reported. This also led to the synthesis electron doped cobaltates [4] using Pulsed Laser deposition using the same principle as that used for the manganites.

In this talk I will present an overview of the current status on the investigations on electron doped manganites and related systems.

References:

1. P. Raychaudhuri, S. Mukherjee, A. K. Nigam, J. John, U. D. Vaisnav, R. Pinto, and P. Mandal, J. Appl. Phys. **86**, 5718 (1999).

2. C. Mitra, Z. Hu, P. Raychaudhuri, S. Wirth, S. I. Csiszar, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. B **67**, 092404 (2003).

3. C. Mitra, P. Raychaudhuri, K. Dörr, K.-H. Müller, L. Schultz, P. M. Oppeneer, and S. Wirth, Phys. Rev. Lett. **90**, 017202 (2003).

4. D. Fuchs, P. Schweiss, P. Adelmann, T. Schwarz, and R. Schneider, Phys. Rev. B **72**, 014466 (2005).

Exploring Novel Magneto-resistive and Transport Properties in Pulsed Laser Deposited Manganite Thin Films

D. G. Kuberkar
Department of Physics, Saurashtra University
Rajkot 360 005
Email: dgk@icenet.net

Abstract

For the past one decade, a significant upsurge in research on ABO3 type manganites is mainly attributed to the application potential of colossal magnetoresistance (CMR) property exhibited by these compounds. Though the realization of applications of these oxides still remains an open question, the compounds continue to attract the scientific community due to the rich physics evolving as a result of spin, charge and orbital degrees of freedom. During this talk , the results of our recent studies, both on tailoring these materials to obtain enhanced magneto-resistance (MR) for applications point of view and on some exotic transport properties at low temperatures, will be presented.

The fabrication of manganite thin films is essential because films could find applications and also help in studying the clean physics in the absence of dominant grain boundary effects. Pulsed Laser Deposition (PLD) is an efficient tool to fabricate the high quality epitaxial thin films of manganite oxides and to grow multilayer structures, which could be evaluated for possible applications. We show that, by controlling the growth parameters, phase-separation may be induced to obtain unusually high MR in A-site disordered $(La,Pr)_{0.7}A_{0.3}MnO_3$ (A=Sr, Ba) manganites. Swift Heavy Ion (SHI) irradiation is another technique employed to induce the controlled defects in the thin films. Our detailed investigations on the SHI irradiation induced modifications in the structural and transport properties of thin films of varying thicknesses reveal that, SHI effect on transport and MR properties gets more pronounced with increasing thickness of the films. In addition to MR properties, we also observed some low temperature transport anomalies arising due to structural disorder in Ba-based compounds. Present talk will highlight some interesting findings of our recent investigations on CMR manganites in the context of all the above-mentioned aspects.

Photonic and Spin-photonic Semiconductor Nanostructures Grown by Pulsed Laser Deposition

Lalit. M. Kukreja
Thin Film Laboratory
Centre for Advanced Technology, Indore – 452 013, INDIA
Email: kukreja@cat.ernet.in

Abstract

This paper reviews our recent research on structural and optical properties of quantum dots of Si, quantum wells and dots of ZnO and thin films of Mn and Co doped ZnO grown by Pulsed Laser Deposition (PLD). A particulate free multilayer structure of Al_2O_3 capped Si quantum dots of different mean sizes grown by an off-axis deposition scheme showed variable band-gap in photoabsorption spectra in line with the putative quantum confinement effects. Room temperature photoluminescence from Si quantum dots grown for different times showed features without any apparent size dependent spectral shift which, albeit has earlier been explained by others originating from the defect levels at the interface of Si and SiO_2 shells surrounding the nanoparticles but still have certain mysteries attached. On the contrary ZnO quantum dots, also capped with Al_2O_3 in multilayer structure, showed size dependent band-gap shifting in photoabsorption spectra in the range from about 3.3 to 4.5 eV when the mean dot radii varied from about 4 to 2 nm. High quality ZnO/MgZnO quantum wells grown by an in-house developed methodology of buffer assisted growth showed a monotonic blue shift of the band-gap from about 3.35 to 3.75 eV both in photoabsorption and photoluminescence when the well thickness decreased from about 5 to 1 nm. These quantum structures are expected to play vital role for the development of future photonic devices.

An equally exciting area of spint-photonics is currently on the horizon. Diluted magnetic semiconductors (DMS) of Mn and Co doped ZnO are being studied extensively to explore if those could be potentially useful for spin-optoelectronic devices. We have synthesized bulk and thin films of these materials with different dopand concentrations. The PLD grown films of a few hundred nm thickness are found to have high crystalline quality and a homogenous wurtzite phase with monotonic increase in the band-gap of the resulting alloy with increasing concentration of Mn and Co in their corresponding films. We have also observed broad mid gap absorption in the photoabsorption spectra of both Mn and Co doped ZnO films. Low temperature photoluminescence of MnZnO alloy films with different concentrations of Mn, showed efficient band edge emission with additional features, which might originate from the clusters of MnO or MnO_2 due to the crystal field transitions of Mn^{2+} ions. Further investigations on the optical and magnetic characteristics of these spin-photonic semiconductor films are under way.

The Evolution of PLD: From High T_c Superconductors to Spintronics

M.S. Ramachandra Rao
Department of Physics and Materials Science Research Centre
Indian Institute of Technology (IIT) Madras, Chennai – 600 036
Email: msrrao@iitm.ac.in

Abstract

Pulsed laser deposition (PLD) has proved to be one of the most versatile techniques to realize high quality thin films of not only oxide materials but also a variety of solid state materials. With a modest beginning as a not-so-popular technique in the sixties [1], it has come to stay, with the advent of high T_c superconductivity [2], as the most profoundly used deposition technique in the past two decades. Applications of the technique include the fabrication of high current density superconducting films, high quality ultrathin gate-dielectric layers, biocompatibility for medical applications, hardware resistant coatings, diamond coatings, production of carbon nanotubes, epitaxial transparent conducting oxide (TCO) films, hydrogen and other gas sensors, films with nanostructured and self-assembled arrays, magnetic multilayers and heterostructures and GMR/CMR based magnetic tunnel junctions (MTJs) and diluted magnetic semiconductors (DMS) for spintronic applications. PLD by virtue of its simplicity scores over other techniques in terms of, *i).* stoichiometric production of films of multicomponent systems, *ii).* relatively high deposition rate (~ 100 Å/min @ moderate laser fulences), *iii).* use of laser as an external energy source to avoid contamination and *iv).* facilitation of multilayer film deposition without breaking vacuum. It is the fastest evaporation (occurring in time scales of few nanoseconds) technique in which the laser produced plasma (plume) expands rapidly away from the target surface with particle velocities typically in the range 10^6 cms^{-1} and kinetic energies of the emanating species ~ 80 eV as compared to 2-10 eV in the case of filament-based-thermal-evaporation. The fundamental aspect of plume generation during the laser-target interaction process is still a matter of intense research.

In this review talk, I will give a brief glimpse of the technique, highlighting salient results pertaining to two research areas, HTSC and manganites, in which PLD was extensively used. I will also highlight the recent trends in PLD to realize nanostructured and self assembled arrays of some oxide systems. I will then talk about the emerging field of spintronics, in the context of oxide electronic materials, which is an emerging field for future spin electronic and quantum computational devices [3,4].

References:

[1]. H.M. Smith and A.F. Turner. Appl.Opt. 4 (1965) 147.

[2]. D. Dijkamp et al. Appl. Phys. Lett. 81 (1987) 619.

[3]. H. Ohno et al. Appl. Phys. Lett. 69 (1996) 363.

[4]. D.D. Awschalom and J.M. Kikkawa. Physics Today, 52 (1999) 33.

Pulsed laser Deposition of Oxides on polymer substrates for Optoelectronic Applications

M.K.Jayaraj*, R.Manoj, R.S.Ajimsha., R.Reshmi
Optoelectronics Device laboratory, Department of Physics,
Cochin University of Science and Technology, Cochin – 682 022.
*Email: mkj@cusat.ac.in

Abstract

Wide band gap oxide films are important component in Optoelectronic devices. Thin films deposited on organic substrates can be used in plastic liquid crystal displays, Transparent electromagnetic shielding material, flexible electro optical devices, solar cells, thin film electro luminescent devices etc. Due to the poor thermal endurance of organic substrates films should be deposited at low substrate temperature. Wide variety of methods, such as sputtering, chemical deposition, and sol gel method are commonly used to deposited oxide films. A high temperature post deposition heat treatment is required to produce crystalline film which is not possible with these organic substrates. In this paper we review the work that we have carried out on ZnO and $ZnGa_2O_4$ thin films grown by pulsed laser deposition. Highly oriented ZnO films and polycrystalline $ZnGa_2O_4$ films were grown by PLD on various substrates like quartz, silicon and organic polymer substrates (kapton HPP-ST polyamide). By controlling the deposition parameters like substrate to target distance, oxygen partial pressure and laser fluence crystalline films were grown on organic substrates at a substrates temperature of 25^0C. The films were characterized by studying the optical, electrical and structural properties. The Photoluminescent emission and excitation of the PLD grown oxide films on organic substrates were also discussed.

Synthesis of Epitaxial AlN thin films by pulsed laser deposition

Ravi Bathe

International Advanced Research Center for Powder Metallurgy and New Materials, Balapur PO, Hyderabad 500 -005, India

Email: ravi@arci.res.in

Abstract

AlN has a large potential to become important in a wide range of applications. Its wide (6.2 eV), direct, band gap combined with well matched structural and thermal properties to SiC makes it an ideal candidate for future MESFET and MISFET SiC-transistors as well as high temperature and high power electronics applications. Due to a small lattice mismatch to SiC (~ 1%), epitaxally grown AlN thin films seem to be promising candidates for dielectric applications and ion-implantation anneal cap. We have investigated the epitaxy, interfaces, surfaces and defects in epitaxial AlN thin films grown on SiC by pulsed laser deposition. The crystalline structure and surface morphology of the epitaxially grown AlN thin films on SiC (0001) substrates have been studied using x-ray diffraction (and scans) and atomic force microscopy, respectively. The defect density and analysis have been studied by using Rutherford backscattering spectrometry, ion channeling technique and transmission electron microscopy. The films were grown at various substrate temperatures ranging from 500 to 1100 ^{0}C. X-ray diffraction measurements show highly oriented AlN films above growth temperature of 750 ^{0}C, and single crystalline nature above 800 ^{0}C. The films grown in the temperature range of 950 ^{0}C to 1000 ^{0}C have been found to be highly strained, where as the films grown above 1000 ^{0}C were found to be relaxed after crack propagation along the crystallographic axes. We found that during initial stages, growth of a 20 nm thick AlN low-temperature buffer layer is critical for obtaining crack free, smooth, high-quality epitaxial films. By controlling the initial stages of growth in a two-step deposition process, it is shown that high quality epitaxial layers on SiC can be obtained with low intrinsic stresses, good surface morphology, and higher electrical break-dawn strength. The significance of these results towards development of high temperature-high-power electronics is also discussed.

Nanocrystalline Films of Gadolinia Doped Ceria Prepared by Pulsed Laser Ablation

P. Kuppusami
Physical Metallurgy Section
Indira Gandhi Centre for Atomic Research
Kalpkkam-603 102, Tamilnadu
Email : pk@igcar.ernet.in

Abstract

Nanocrystalline oxides are displaying electrical properties which appear to be unique and may lead to applications that are not attainable by conventional microcrystalline oxides. As a result, it is very important to understand the relationship between microstructure and electrical properties as well as to be able to control the microstructure in the nanocrystalline range. New phenomena observed in nanocrystalline oxides are related to the increasing grain boundary volume and in the change of stoichiometry, which may lead to enhance the reaction kinetics and electrical conductivity.

Synthesis of nanocrystalline materials has been carried out most frequently by assembling pre-generated small clusters by means of consolidation and sintering. A variety of cluster generation methods such as sol-gel technique, laser ablation, sputter deposition and precursor spin coating technique have been reported. In comparison with methods such as consolidation and sintering of clusters, the latter techniques are the low temperature methods, which have significant advantage. Pulsed laser ablation is a unique technique where the deposition is not only carried out at low substrate temperatures, but also the stoichiometry of the target is retained in the ablated films. The technique is also capable of depositing metastable materials that are difficult to synthesize in bulk form by other deposition methods. These features enable to control the grain size and to obtain stable microstructure and make it possible to study microstructure-property relationships.

In the present work, microstructure of thin films of gadolinia doped ceria (GDC) prepared by pulsed laser ablation is investigated. The growth characteristics of the films as a function of substrate temperature, oxygen partial pressure and laser energy are investigated using the techniques of x-ray diffraction and electron microscopy. The influence of growth induced defects on the ionic conductivity of the doped ceria will be highlighted.

Pulsed Laser Ablation grown Relaxor based bilayers, multilayers and heterostructures for multiferroic applications

R. Ranjith* and S. B. Krupanidhi
Materials Research Centre, Indian Institute of Science, Bangalore-560 012
*Email: ranjith@mrc.iisc.ernet.in

Abstract

Ferroelectric heterostructure like super lattices and multilayers have shown superior properties and have been the interest of study in the recent years[1]. The interfaces present and the size of the individual layers present play a crucial role in these heterostructure. In this work multilayer of PMN-PT with varying composition of PT across the film was fabricated using pulsed laser ablation technique. Samples with varying individual layer thickness were fabricated to study the size dependent behavior of these multi-layer thin films. Multilayer films with individual layer thickness of 10,20,30,50,70 and 100nm were fabricated. Polarization studies were carried out on these films with a multilayer structure. A field driven antiferroelectric to ferroelectric transition was observed in the films of individual layer thickness greater than 50nm. The dominance of the interaction between the adjacent layers via the interfacial coupling dominates at low fields to stabilize the antiferroelectric coupling and the dominance of the external field coupling with the individual layers stabilizes the ferroelectric behavior of these films. Figure 1. shows the field driven ferroelectric polarization. Films with low individual layer thickness exhibited ferroelectric behavior and on increase of individual layer thickness they exhibited an anti-ferroelectric behavior and on further increase of thickness they showed a weak anti-ferroelectric followed by a weak ferroelectric behavior on further increase of thickness. This phenomenon is attributed to the long-range coupling observed in these materials[2], which gives an averaged property, and on increase of thickness they behave as individual materials put together. Figure 2. shows the size induced antiferroelectric polarization behavior.

Artificially grown superlattice structures have been an interest of study due to their striking properties both in technological point of view and fundamental physics aspects. In this work superlattices based on $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) – $PbTiO_3$ (PT) were deposited through pulsed laser ablation deposition with different periodicities (10,20,30,40,50,60 and 70nm) for a constant total thickness of the film. The presence of superlattice reflections in the X-ray diffraction pattern clearly shows the superlattice behavior of the films. Polarization hysteresis and the Capacitance – Voltage characteristics of these films shows a clear size dependent Ferro and Antiferro characteristics. Presence of long range coupling in superlattices with lower periodicities (<10nm) exhibited a clear ferroelectric behavior similar to a solid solution of PMN and PT[3]. Superlattices with higher periodicities (20-50nm) exhibited antiferroelectric behavior, which could be understood from the energy arguments. On further increase of periodicities they again exhibited ferroelectric behavior. On increase of temperature beyond the Curie point of PMN the interaction is changed to a Ferroelectric – Paraelectric interlayer interaction and loses its antiferroelectric behavior. The Capacitance –Voltage characteristics and its temperature is given in figure 3.

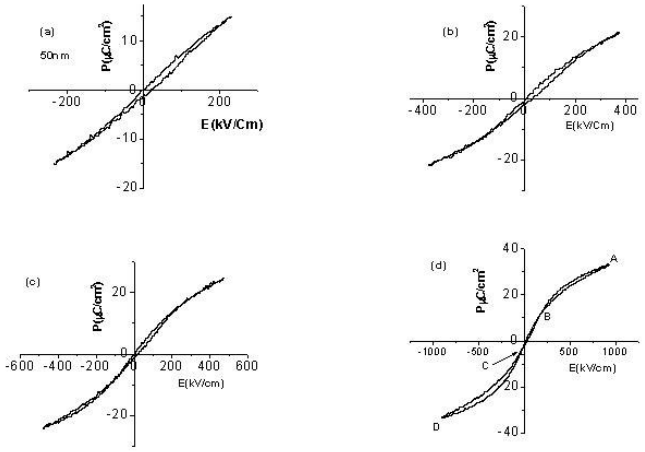


Figure 1. Field driven Antiferroelectric to Ferroelectric transition.

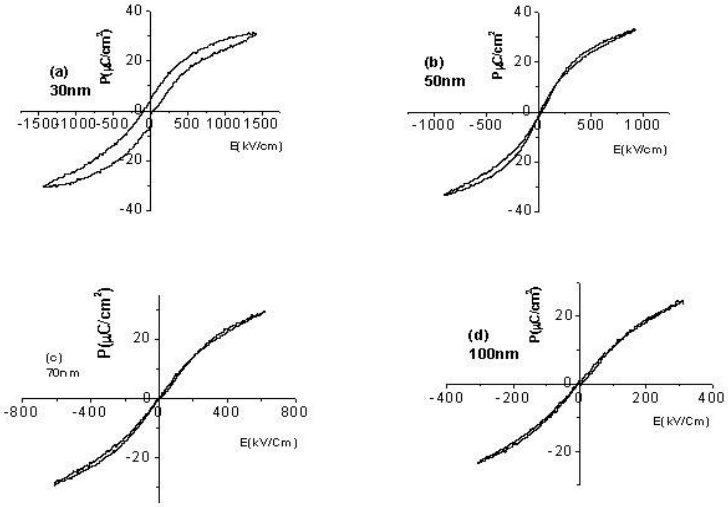


Figure 2. Size driven Antiferroelectric characteristics.

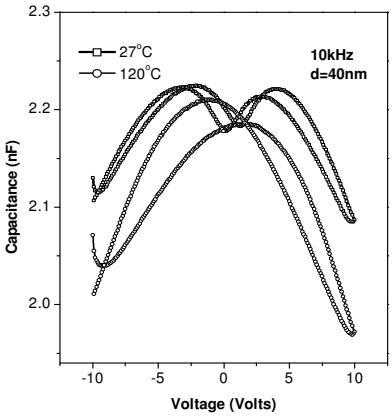


Figure 3. CV characteristics of a PT-PMN superlattice

Major References

1. G.Rijnders and Dave.H.A.Blank, Nature, **433**, 369 (2003).

2. H.M.Christen,E.D.Specht, D.P.Norton, M,F,Chisholm and L.A.Boatner, Appl.Phys.Lett., **72**,2535,(1998).

3. Jian Shen and Yu-qiang Ma, Phys. Rev.B, **61(21)**, 14279, (2000).

Optical Quantum Confinement Effects in ZnO/MgZnO Multiple Quantum Wells Grown by Pulsed Laser Deposition

P. Misra*, T. K. Sharma, S. Porwal and L. M. Kukreja
Thin Film Laboratory, Centre for Advanced Technology, Indore 452 013
*Email: pmisra@cat.ernet.in

Abstract

Current worldwide interest in ZnO as a semiconductor to evolve futuristic optoelectronic, spintronic and other devices has spurred rigorous research on its quantum structures [1]. We have grown ZnO Multiple Quantum Well (MQW) structures on (0001) Sapphire substrates by Pulsed Laser Deposition using a third harmonic of Q-switched Nd: YAG laser. A 10 layer MQW structure was grown with 8 nm thick ternary alloy $Mg_{0.16}Zn_{0.84}O$ layer with a band gap of ~ 4.1 eV as a barrier and the active layer of ZnO had variable thickness in the range of 5 – 1 nm . Prior to the growth of MQWs a 50 nm thick ZnO buffer layer was grown at 750°C, which provided a highly crystalline, smooth and oxygen terminated template for subsequent growth of nanostructures at a lower temperature [2] of 600°C. This low temperature growth ensured chemically sharp interfaces while the high crystalline quality was facilitated by the high temperature grown buffer layer. Room temperature absorption spectra of MQW structures showed two prominent peaks due to excitonic transitions with in the well and barrier layers. The ZnO absorption edge shifted monotonically towards blue with decreasing well layer thickness up to 1 nm due to putative size dependent quantum confinement effects. Photoluminescence (PL) measurements carried out on all the quantum wells at 10K and room temperature using a He-Cd laser to further strengthen our observation. Room temperature PL in the UV spectral range was observed for the MQW samples up to 2 nm of well thickness bellow which the PL signals was too weak to be detected by our PL setup. It is worth mentioning here that the minimum thickness of ZnO QW grown on sapphire by us which showed quantum confinement effect is 1 nm, which is better than reported by Ohtomo et al which was 1.7 nm. Ohtomo et al also could not observe room temperature PL observed by us. All the samples showed strong PL at 10K due to excitonic recombination in ZnO QW. PL spectra of these samples showed a clear blue shift in the ZnO band edge from ~ 3.4 to ~ 3.7 eV with decreasing well layer thickness. The FWHM of PL peak was found to increase monotonically with decreasing well layer thickness probably due to fluctuation in the well layer thickness which is more pronounced at lower thickness of QW. The band gaps obtained from the experimental PL data at 10K were compared with the theoretically calculated values by using one dimensional square well potential approximation and a band offset ratio, $\Delta Ec:\Delta Ev$ of 9:1. Both were found to be in good agreement. Further experiments are underway to investigate the interface quality and to measure the accurate thickness of the quantum wells and to include size dependent variation of the excitonic binding energy in theoretical calculations.

References:

1. A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, M. Kawasaki, Nature Materials, 4, 42-46, (2005)
2. P. Misra and L.M. Kukreja, Thin Solid Films, 485, Issues 1-2, 42-46 (2005)
3. A. Ohtomo, M. Kawasaki, I. Ohkubo, H. Koinuma, T. Yasuda, Y. Segawa, Appl. Phys. Lett. 75, 980 (1999)

High-pulse energy excimer lasers for precise material ablation

Burkhard Fechner and Ralph Delmdahl
Coherent Lambda Physik GmbH, Hans-Boeckler-Str. 12, D-37079 Goettingen, Germany
Email: bfechner@lambdaphysik.com

Abstract

Pulsed excimer lasers are the strongest and most efficient laser sources in the ultraviolet spectral region. Record short wavelengths from 351 nm down to 157 nm as well as record high 1200 mJ pulse energy as available for the 248 nm excimer lasers are commercially provided for numerous laser material ablation approaches. Virtually no material is able to withstand the high photon energies ranging from 3.5 to 7.9 eV emitted by excimer lasers. As a result of the irradiation of material with high energy excimer laser photons at sufficient fluence immediate bond breaking due to electronic excitation is induced. In combination with short-term laser material interaction of only 10 to 30 ns excimer pulse duration, material ablation proceeds via fast vaporization and consecutive ejection of material with only negligible dissipation of heat transfer to the surrounding zone. The effect is an inherently precise and clean ablation quality. Latest developments in excimer laser technology with particular respect to pulsed laser deposition as well as applications will be discussed.

Pulsed laser ablation at the liquid solid interface

D. M. Phase
UGC-DAE Consortium for Scientific Research, Khandwa Road, University Campus, Indore-452 017.
Email: dmphase@csr.ernet.in

Abstract

Pulsed laser ablation (PLA) is a well-known method to produce thin films by ablating material from a solid target of known composition[1]. PLA usually occurs in vacuum or in a background of inert gas or reactive gas. Very recently, PLA at the liquid/solid interface, a new variation of PLA has been reported by Simakin et al[2]. Earlier the concept of pulsed laser induced liquid solid interfacial reaction was used to prepare surface alloys and compounds, which are in the metastable states[3]. Now this novel LP-PLA technique which is also based on same concept has been used to produce a variety of materials, including diamond like carbon films, nanocrystals of carbon nitride and nano meter size particles of Ti, Ag, Au, Si and TiC. This technique shows a great potential as route to novel nano-crystalline materials. However this technique is still in its infancy with much of the parameter space yet to be investigated. In this talk a basic concept of pulsed laser reaction at liquid/solid interface will be described along with some examples of synthesis of metastable compounds. This will be followed by a detailed description of LP-PLA technique with examples of synthesis of nano-structures and nano-particles.

References:

1. R.K.Singh and J.Narayan, Phys.Rev.B 41 (13) (1990) 8843
2. A.V.Simakin, G.A.Shafeev, E.N.Loubnin, Appl. Surf. Sci. 154 (2000) 405.
3. P.P.Patil, D.M.Phase, S.V.Ghaisas, S.K.Kulkarni, S.M.Kanetkar and S.B.Ogale, Phys.Rev.Lett 58(3) (1987) 238.

Pulsed laser deposition of ZnO and Silicon thin films

V. Narayanan and R. K. Thareja
Department of Physics and Centre for laser Technology, Indian Institute of Technology – Kanpur
Email: vnara@iitk.ac.in

Abstract

The thin films of zinc oxide (ZnO) and silicon (Si) were deposited employing reactive and nonreactive pulsed laser deposition technique under various ambient gas conditions of oxygen and helium respectively. The thin films were characterized by atomic force microscopy (AFM). The deposited films were studied using photoluminescence (PL). The work on second harmonic generation (SHG) and third harmonic generation (THG) in ZnO thin films will be discussed. ZnO targets were ablated in ambient oxygen and vacuum using 355 nm third harmonic of Nd:YAG laser with the pulse width of 5 ns and repetition rate of 10 Hz. Laser was focused onto the rotating cylindrical target and plume is emitted normal to the surface and a thin film deposited on the quartz substrate which was kept at 4 cm from the target. The role of zinc and oxygen species on the reactive pulsed laser deposited ZnO films in the ambient oxygen and vacuum was investigated by studying the spatial and temporal evolution of ZnO plasma using optical emission spectroscopy and imaging techniques. Spatially resolved emission spectra showed the abundance of Zn I at 100 mTorr and Zn II at 900 mTorr ambient oxygen respectively. The temporally resolved 2D-images of the expanding ZnO plume were recorded in the ambient gas environment using *intensified*-CCD (ICCD) and the distance – time (R-t) plot from the recorded images followed shock model of the form $R(t) = at^n$ (n = 0.36 at 100 mTorr and n = 0.4 at 900 mTorr of oxygen), where a is a constant. ZnO thin films were deposited at ambient oxygen pressure of 100 and 900 mTorr and an attempt is made to correlate the spectroscopic observations with that of film properties. The films were deposited at room temperature. Surface morphology of the films were carried out using AFM and showed dependence on oxygen pressure. To investigate the non-linear properties of ZnO thin films, harmonic generation (SHG and THG) were performed in the deposited films. The second harmonic co-efficient ($\chi_{eff}^{(2)}$) and third harmonic co-efficient ($\chi^{(3)}$) were 3.2 pm/V and 0.9 x 10^{-12} esu respectively for the films deposited at 100 mTorr oxygen. The third harmonic generated at varying input intensity of fundamental wavelength showed cubic dependence on intensity. A third harmonic (355 nm, pulse width 5 ns FWHM) at pulsed repetition rate of 10 Hz of a Q-switched Nd:YAG laser was used for creating silicon plasma both in vacuum and ambient helium gas. For the thin film deposition of silicon, silicon and quartz substrates were kept close to the target and the helium gas was used for condensation of the nanoclusters in the gas phase. The particle size distribution in the deposited films was analyzed using AFM. The mean cluster size ranging from1.8 nm to 4.4 nm is observed that depended on the laser intensity. To investigate PL properties of the nc-Si films, the films were optically pumped by third harmonic (355 nm) of the Nd:YAG (1064nm) laser. The PL spectra of the silicon thin films showed three distinct emission bands at 2.7, 2.2, and 1.69 eV.

Pulsed laser deposited, highly c-axis oriented GaN thin films for field emitter applications

S. M. Jejurikar*, A. V. Limaye and K. P. Adhi

Advanced Laser Material Processing Laboratory, Centre for advanced studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune -411 007, India

P. M. Koinkar, M. A. More, and D. S. Joag

Field ion microscopy and Field emission spectroscopy Laboratory, Centre for advanced studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune -411 007, India

L. M. Kukreja

Thin Film Laboratory, Center for Advanced Technology, Indore – 452 013, India

*Email: suhas@physics.unipune.ernet.in

Abstract

Realizing GaN in highly oriented / epitaxial thin film form is currently a subject of active research interest. This interest stems from the fact that GaN is potentially an important material for applications like UV-visible light emitting device (LED), laser diodes, detecting devices, high temperature / high power electronics etc[1-3]. Further, the lattice mismatch between GaN/ZnO and GaN/AlN is ~ 2 % and ~ 4 % respectively, suggesting that the thin films of GaN could be ideal buffer layers for the epitaxial / highly oriented growth of AlN wide band gap semiconductor films, for which no suitable low cost substrates are presently available. Here, we explore the possibility of using GaN thin films for applications based on cold emission. We also discuss the field enhancement factor, stability of emission etc. However in such applications, it is imperative to grow good quality thin films of GaN especially on substrates of the most used electronic material i.e. Silicon (Si) albeit it is totally lattice mismatched. GaN thin films were grow on Si/SiO_x substrates by PLD. Excimer-laser (KrF gas; wavelength □ = 248 nm, pulse duration t_p = 20 nsec, repetition rate = 10Hz) was used for the ablation of the GaN target which was synthesized in-house using 99.999% purity GaN powder (Aldrich Sigma). The laser fluence on the target surface was kept at 1.5 J/cm^2. Base vacuum in the chamber was of the order of 1 x 10^{-6} Torr. High purity (99.999%) nitrogen was introduced into the deposition chamber and the pressure was maintained at 5 x10^{-5} Torr throughout the deposition. The depositions were carried out at substrate temperature of 800 °C for duration of 1200 sec.

Inspite of large lattice mismatch (16 %), high thermal mismatch[4-6] (~ 54%) and the large difference in the crystal structure, highly c-axis oriented growth of GaN has been successfully obtained on Si / SiO_x substrate. This is clearly evident from the presence of (0002) plane of GaN in the XRD pattern. The FWHM of the (0002) peak is estimated to be ~1.0^o suggesting a highly strained film which is obvious. The surface morphology, as seen by AFM, however does not show any cracks in the films, which is encouraging. The rms surface roughness of the films is ~ 3.5 Å.

The field emission current-voltage (I-V) characteristics were recorded at a base pressure of 10^{-6} Torr. Field emission current of ~ 30 nA was obtained at an applied voltage of 2.8 kV. Linear relationship in the corresponding

Fowler-Nordheim (F-N) plot of log (I/V^2) versus $10^4/V$ confirms that the current is due to field emission[7]. The field enhancement factor β can be calculated using formula

$$\beta = [\, 2.97 \times 10^3 \times \Phi^{3/2}] / m$$

where Φ is the work function of GaN (4.995 eV) and m is the slop of F-N plot. The β factor in our case is estimated to be 28,931 cm^{-1}. High β factor is desirable for devices using cold emission.

Acknowledgement: The authors KPA, AVL, LMK and SMJ would like to thank DAE- BRNS for the financial support extended for carrying out this work under the project sanction No. (2002/34/21/BRNS).

References:

1. A. Castaldini, A. Cavallini, and L. Polenta, Appl. Phys. Lett. **87**, 122105 (2005)
2. M. A. Reshchikov and H. Morkoc, Appl. Phys. Lett. **97**, 061301 (2005)
3. S.Ito, J. Ohta, H. Fujioka, M. Oshima, Appl. Surf. Sci. **197 -198**, 384 (2002)
4. Srinivasan Raghavan, Xiaojun Weng, Elizabeth Dickey, and Joan M. Redwing, Appl. Phys. Lett. **87**, 142101 (2005)
5. A. Krost, A. Dadgar, G. Strassburger, and R. Clos, Phys. Status Solidi A **200**, 26 (2003)
6. L. Macht,a_ P. R. Hageman, S. Haffouz, and P. K. Larsen, Appl. Phys. Lett. **87**, 131904 (2005)
7. V. N. Tondare, C. Balasubramanian, S. V. Shende, D. S. Joag, V. P. Godbole,, S. V. Bhoraskar, M. Bhadbhade,, Appl. Phys. Lett. **80**, 4813 (2002)

Growth and characterization of excimer laser-ablated bismuth vanadate ($Bi_2VO_{5.5}$) thin films

Neelam Kumari*, K.B.R. Varma, S.B. Krupanidhi
Materials Research Centre, Indian Institute of Science, Bangalore-560 012
*Email : neelam@mrc.iisc.ernet.in

Abstract

Ferroelectric thin films have become increasingly important as future materials for electronic devices. Ferroelectric random access memory (FeRAM) has been developed as an ultimate memory with both nonvolatility and a high-speed read /write operation cycle, which have been quite difficult to attain in conventional fast static (SRAM) or electrical erasable programmable read only memories (EEPROM)1. Bismuth based layered ferroelectric compounds are being considered as potential candidates for memory devices due to their better fatigue characteristics2. Bismuth vanadate Bi2VO5.5 (BVO) is a vanadium analogue of an n=1 member of Aurivillius family, [Bi2O2]2+[An-1BnO3n+1]2- of oxides3.Bismuth vanadate, Bi2VO5.5 (BVO) is one of the most promising ferroelectric materials owing to its low relative dielectric constant and requirement for low deposition temperature to grow an epitaxial thin film4. Pulsed laser ablation technique has been employed to deposit the polycrystalline thin films of layered -structure ferroelectric Bi2VO5.5 (BVO) on Pt coated Si substrates. The effect of oxygen pressure on the growth of BVO thin films has been studied by depositing the thin films at different pressures. The substrate temperature was optimized to be 6500C to obtain crystalline films. Figure 1.shows the x-ray diffraction pattern of BVO thin films at different oxygen pressures. The strong and sharp Bragg peaks indicate that the pulsed laser ablation-grown films were highly textured and possessed high degree of crystallinity. Scanning electron microscopy (SEM) was employed to study the microstructure and the cross-sectional SEM images revealed a densely packed grains across the film and the same was used to estimate the thickness of the film. Figure 2a and2b shows the surface and cross-sectional SEM micrograph respectively and the thickness of the film estimated was around 600□30nm. The electrical properties were studied in Metal-Insulator-Metal configuration. Ferroelectricity of the films was verified by examining the polarization with the applied electric field and was also confirmed from the capacitance voltage characteristics (C-V). Figure 3a and 3b shows the polarization hysteresis and the capacitance-voltage characteristics of the film deposited at 6500C. The film exhibited well-defined hysteresis loops, and the values of saturation (Ps) and remnant (Pr) polarization were 7.89□C/cm2 and 3.09 □C/cm2, respectively. Figure 4 shows the dielectric constant and loss as a function of frequency at room temperature. The room temperature dielectric constant and dissipation factor were 88 and 0.7, respectively, at a frequency of 100kHz. The charge transport in terms of oxygen ion vacancy migration and dielectric relaxation phenomena are the most important characteristics for any oxide thin film device, for practical as well as scientific reasons. These phenomena will be discussed.

Pyramidal Nanostructures of ZnO

S. Angappane,* Neena Susan John and G. U. Kulkarni
Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore - 560 064, INDIA.
*Email: angappan@jncasr.ac.in

Abstract

Nanostructures of Zinc oxide have received considerable attention.[1,2] Pulsed laser deposition (PLD) is a versatile technique which has been used to obtain nanowires and nanorod arrays of ZnO.[3] We have sought to prepare ZnO nanostructures on silicon substrates using PLD under different deposition conditions and find their hardness and gas sensing characteristics. We report here an unusual growth of ZnO in the form of well-defined pyramidal nanostructures grown on a thin film of the same material.

A frequency tripled pulsed Nd:YAG laser (Quanta-Ray GCR-170, Spectra-Physics, USA) with a pulse width of ~ 5 ns and repetition rate of 10 Hz was used for the ablation of ZnO target. A convex lens of 50 cm focal length was used to focus the laser beam on to the target, through a quartz window fastened to the deposition chamber, held at 10^{-6} Torr. The substrate, Si(100) was placed directly opposite to the target at ~ 5 cm, fastened to a molybdenum boat whose temperature could be varied up to 1500 ºC. Prior to mounting, the silicon substrate was cleaned using the piranha solution (1:2 H_2O_2:H_2SO_4) (Caution: this mixture reacts violently with organic matter) and etched in HF (1:10 HF:H_2O). The energy of the laser was optimized at 200 mJ per pulse to enable the desired growth of the nanostructures. The deposition was made at different substrate temperatures (600 ºC and 900 ºC) and for different deposition times (15, 30 and 45 minutes) under a pressure of 10 mTorr of oxygen.

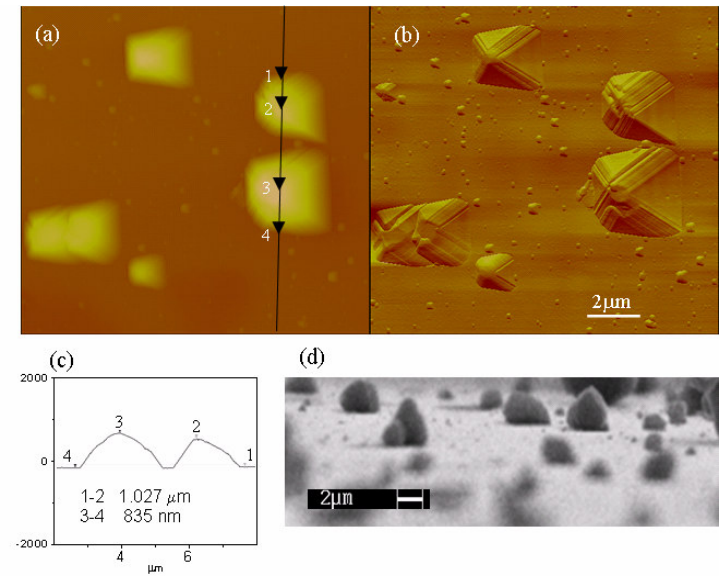


Figure 1: AFM images of ZnO deposited for 45 minutes on a Si(100) surface held at 600ºC: (a) height image (b) friction image. (c) Profile analysis of the image in (a), (d) SEM image of the nanostructures collected with the substrate oriented at ~ 5º to the beam.

Atomic force microscope (AFM) and scanning electron microscope (SEM) images of the ZnO nanostructures obtained after 45 minutes of deposition on the Si(100) surface held at 600 ºC, are shown in Figure 1. The topography and friction images shown in Figures 1 a and b respectively reveal complimentary details of the nanostructures. While the presence of micron-sized structures is apparent from the topography image (Fig. 1a), their pyramidal morphology is revealed by the friction image in Figure 1b. The facets and the associated fine structures with sharp edges are clearly seen in the friction image. The line-profiles of two of the nanostructures in Figure 1c provide a base width of ~ 2 μm and a height of ~ 1 μm. The SEM image shown in Figure 1d, contains several such pyramidal structures. Imaging in larger areas has shown that the pyramidal structures vary in a narrow size range of 1.5 to 2 μm. AFM images show a few small features after 15 minutes of deposition and a longer deposition for 30 minutes clearly produces larger and more number of structures of pyramidal morphology. Though pyramid-like surface roughness has been reported,[4] the pyramids observed in this work are unique in that they exhibit well defined ordered growth of pyramidal nanostructures. By employing a higher substrate temperature of 900 ºC, we could obtain a higher density of ZnO structures in the form of hexagonal islands.

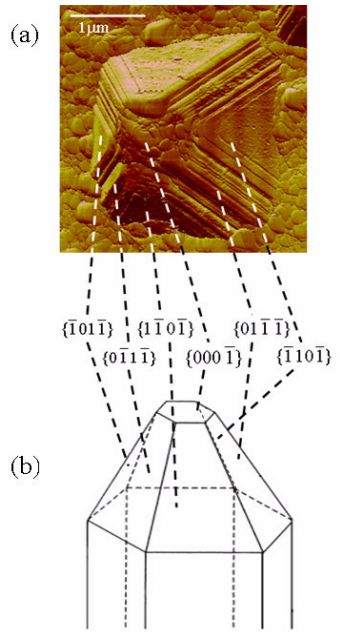


Figure 2: (a) AFM image of a single pyramid (b) Growth habit of ZnO.

The pyramidal morphology of ZnO nanostructures can be explained based on the growth habit of ZnO, as illustrated in Figure 2. The growth rates of different faces of ZnO bear the following relation: $V_{<0001>} > V_{<01\bar{1}\bar{1}>} > V_{<0\,1\,\bar{1}\,0>} > V_{<01\bar{1}\,1>} > V_{<000\bar{1}>}$.[5] It may be noted that a crystal face whose growth is relatively fast would eventually disappear giving space to a face that grows at a slower rate. Thus, the $\{0\,\bar{1}\,1\,\bar{1}\}$ and $\{01\,\bar{1}\,\bar{1}\}$ faces having higher growth rates have almost disappeared resulting in a four faced pyramid structure (see Fig. 2). Such a structure perhaps belongs to an intermediate state in the growth of hexagonal nanorods reported by others.[3] X-ray diffraction from the sample containing pyramidal nanostructures showed a prominent peak corresponding to the (002) plane, thereby implying a highly oriented nature of the nanostructures. As can be seen from Figure 1, the edges along the

base of the pyramids are oriented along the axes of Si. The oriented pyramids of ZnO could be due to matching of domains of 5 unit cells of ZnO (a, b = 3.25 Å) with 3 unit cells of Si (a = 5.43 Å).

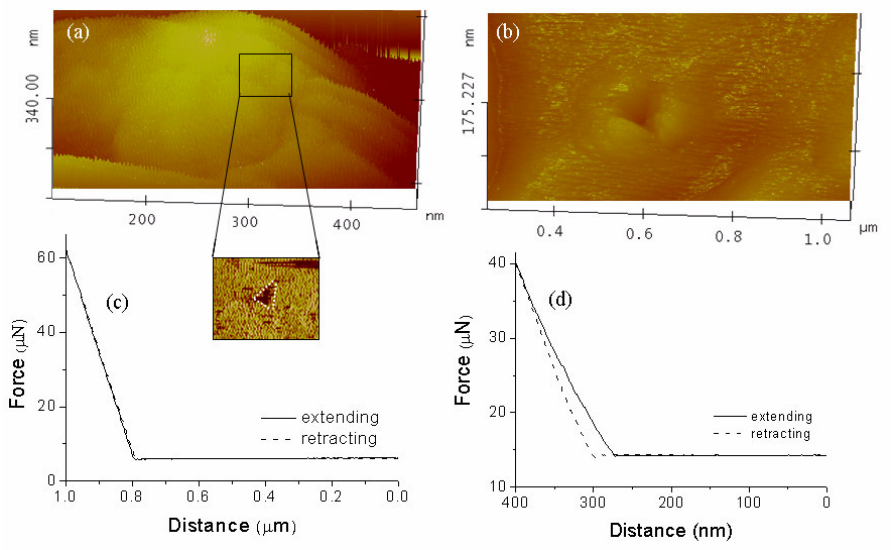


Figure 3: Nanoindentation on (a) ZnO pyramid and (b) surface of the ZnO film on Si(100). Inset of (a) shows the phase image of the indented region. The corresponding force-distance curves are shown in (c) and (d). Hysteresis in F-D response is an indication of deformation.

The force-distance response following nanoindentation on a ZnO pyramid is shown in Figure 3 along with that from the film surface. The projected area of the indent was calculated from the AFM images. The projected area of the indent on the pyramid (770 nm^2) is much less than that on the plane surface (4330 nm^2). The hardness value comes out to be 70 ± 10 GPa for the pyramid, in contrast to 6 ± 0.5 GPa for ZnO film.[6] The increased hardness for ZnO nanorods could be due to the increased surface energy relative to bulk.

Using conducting AFM measurements,[7] the gas sensing properties of the pyramidal structures were studied while controlling the flow of oxygen. In an oxygen atmosphere, the current decreases for positive bias voltages, due to depletion of electrons from the conduction band due to adsorbed oxygen ions. By holding the AFM tip engaged while leaking oxygen into the environmental hood, upto 70% variation in the resistance was obtained from a pyramid.

References

1. Z.L. Wang, Materials Today **7**, 26 (2004).
2. C. N. R. Rao, F. L. Deepak, G. Gundiah and A. Govindaraj, Progr. Solid State Chem. **31**, 5 (2003).
3. Y. Sun, G. M. Fuge and M. N. R. Ashfold, Chem. Phys. Lett. **396**, 21 (2004) and references therein.
4. E. Vasco, C. Zaldo and L. Vázquez, J. Phys.: Condens. Matter **13**, L663(2001).
5. W. –J. Li, E. –W. Shi, W. –Z. Zhong and Z. –W. Yin, J. Crystal Growth **203**, 186 (1999).
6. V. A. Coleman, J. E. Bradby, C. Jagadish, P. Munroe, Y. W. Heo, S. J. Pearton, D. P. Norton, M. Inoue and M. Yano, Appl. Phys. Lett. **86**, 203105 (2005).
7. N. S. John and G. U. Kulkarni, J. Nanosci. Nanotech. **5**, 587 (2005).

Synthesis of novel lithiated transition metal oxide thin films for microbattery application

O.M.Hussain
Thin Film Laboratory, Department of Physics, Sri Venkateswara University, Tirupati-517 50,
Email: hussainom48@yahoo.co.in

Abstract

Introduction: Advances in microelectronic industry, in particular, the development of micro-electromechanical systems (MEMS) technology, have reduced the current and power requirements to extremely low levels. This has prompted the development of all solid state thin film microbatteries as light weight, noise free and compact power sources. The realization of such thin film batteries originate from the identification of new thin film cathode materials with high energy density, high specific capacity and structural stability towards lithium insertion. The most recent candidates are a family of lithiated transition metal oxides (TMO) [1,2]. These compounds exhibit high potentials (>4V) with lithium anode, structurally stable in fully lithiated state and can show very good reversibility. The synthesis of these compounds in thin film form is of great interest as a result of their possible use as a binder free positive electrode in all solid state microbatteries to power microelectronics. In the fabrication of TMO films, the formation of open structure is found to be more crucial. The low temperature synthesis provides smaller grain size and high surface area that greatly improves the cell performance. Recently the pulsed laser deposition technique has been widely recognized as a very promising, versatile and efficient method in the growth of high quality films from a variety of materials even containing volatile components with complex stoichiometry [3]. For this reason, it is a well suited for the growth of transition metal oxide thin films compared to other conventional evaporation techniques where lithium loss occurs due to volatilization. Hence in the present investigation, thin films of lithiated transition metal oxides such as $LiCoO_2$ and $LiMnO_2$ were prepared by pulsed laser deposition technique. The structure and surface morphology of these films were studied as a function of deposition parameters. The electrochemical behavior of these films were studied by investigating the charge – discharge profiles for their effective utilization as cathode materials in microbattery applications.

Experimental: Thin films of $LiCoO_2$ and $LiMnO_2$ were prepared by pulsed laser deposition technique on silicon substrates. The targets were prepared from high purity powders pressed at 5 tons/cm^2 to make pellets of 3 mm thickness and 13 mm diameter and sintered at 800 ^{o}C for 10 hrs. The target was rotated at 10 rotations per minute to avoid depletion of material at the same spot. A KrF excimer laser with a wavelength of 248 nm was used to ablate the target with an energy density of 300 mJ with a pulse repetition rate of 10 Hz. The distance between the target and the substrate was typically 4.0 cm. The films were deposited at various substrate temperatures (100 – 600 ^{o}C) and oxygen partial pressures (50 – 200 mTorr).The structure of the films was studied by a Seifert X-ray diffractometer with a nickel filtered CuK_α radiation (λ = 1.5406 Å). The surface morphology of the films was studied by atomic force microscopy (Digital instruments, 3100 series). The electrochemical measurements were carried out using galvanostatic mode of a Mac-pile system in the potential range 2.0 – 4.2 V.

Results and discussion: Pulsed laser deposited films were found to pin hole free and well adherent to the substrate surface. The influence of oxygen partial pressure (pO_2) and substrate temperature (T_s) on the structure and surface morphology of the films was studied. The electrochemical properties of these films were studied.

$LiCoO_2$ thin films: The X- ray diffraction patterns of $LiCoO_2$ thin films grown on silicon substrates maintained at a substrate temperature of 300 ^{o}C in an oxygen partial pressure of 100 mTorr from a target without Li_2O additive displayed the presence of two additional small peaks at 2θ = 45 and 59 ^{o} along with the peaks at 2θ = 18.95 and 38.48 ^{o} which can be attributed to the presence of cobalt oxide impurities (Co_3O_4 Phase) due to lithium deficiency [4].

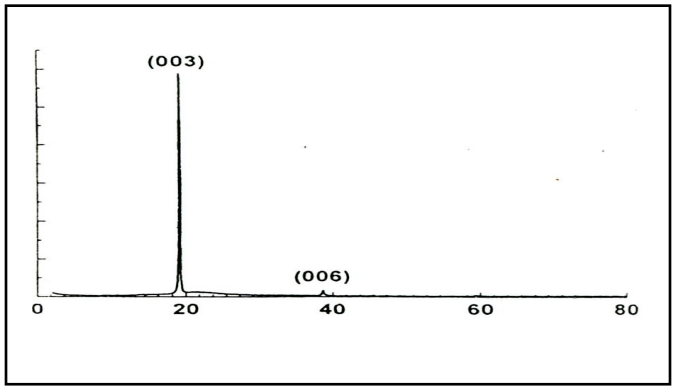


Fig. 1 XRD pattern of $LiCoO_2$ thin film deposited at T_s = 300 °C in pO_2 = 100 mTorr

the $LiCoO_2$ + 10% of Li_2O target. The films exhibited only two peaks at 2θ = 18.95 and 38.48 ° which are indexed as the (003) and (006) reflections (Fig.1) respectively, of hexagonal $LiCoO_2$. The other reflections such as (101), (012) and (104) which were usually observed for $LiCoO_2$ powder samples were not observed in XRD pattern. This indicates that the film has a preferred c-axis (00l) orientation perpendicular to the substrate surface. In fact, this is the advantage of pulsed laser deposition for the growth of oriented films at low temperatures when compared to other physical deposition methods like electron beam evaporation. The AFM data demonstrated that the films deposited at 300 ° C are homogeneous and uniform with regard to the surface topography and thickness over an area of 1 cm^2. The surface topography reveals that the film is composed of roughly spherical grains of varying sizes and the estimated average grain size was found to be 80 nm with a root mean square surface roughness of about 6 nm. The individual grains are clearly visible and are seem to be in good contact with each other. The films exhibit characteristic open and porous structure with small grains when deposited at low substrate temperature (300 °C) and are highly useful as cathode materials.

The electrochemical properties of $LiCoO_2$ films were tested by fabricating an electrochemical cell with 1 M $LiClO_4$ in propylene carbonate as an electrolyte and Lithium as an anode. The electrochemical measurements were carried out at a rate of C/100 in the potential range 2.0 - 4.2 V. Typical charge-discharge curves of Li//$LiCoO_2$ cell is shown in Fig.2. The electrochemical process is seems to be a classical intercalation mechanism for lithium ions into Li_xCoO_2 matrix. In the high voltage region, the cell delivers a specific capacity of 195 $mC/cm^2.\mu m$.

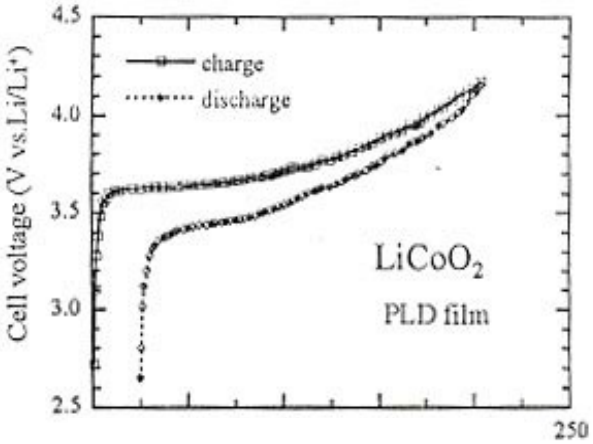


Fig. 2 Charge Discharge profile of Li / $LiCoO_2$ cell

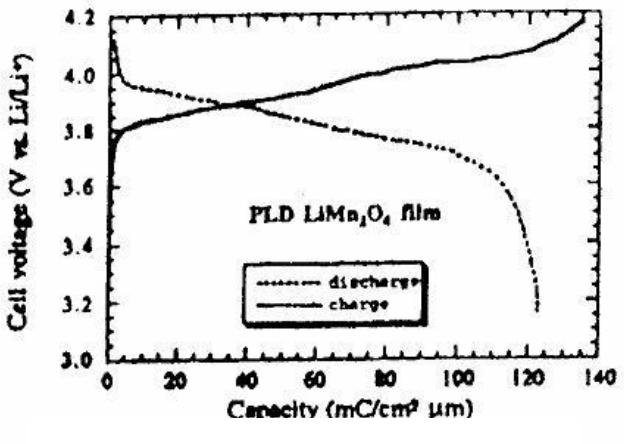


Fig. 3 Charge Discharge curves of a Li / $LiMn_2O_4$Microbattery

$LiMn_2O_4$ films: Thin films of $LiMn_2O_4$ were prepared by pulsed laser deposition technique onto well cleaned silicon wafers maintain at 300 ° C in an oxygen partial pressure of 100 mTorr from a target of $LiMn_2O_4$ in which the Li/Mn ratio was 1.1. The X-ray diffraction pattern displays peaks at 2θ = 16.1, 35.9 and 47.2 ° which are attributed to the (111), (311) and (400) Braggs lines of regular spinel

structure [5]. The surface morphological data of these films demonstrated that the film consists of uniform spherical grain with an average grain size of 50 nm. The films were used as cathode materials and tested in lithium microbatteries with 1 M $LiC1O_4$ in propylene carbonate as an electrolyte. The charge and discharge curves of $Li//LiMn_2O_4$ were tested in the potential region 3.0 – 4.2 V at a rate of C/100 (Fig.3). An initial voltage of about 3.4 V vs. Li/Li^+ was observed for the $LiMn_2O_4$ thin film cathode cells. The cell voltage profiles displayed several plateaus and the voltage of each plateau is a function of structural arrangement. In the high voltage, region the cell delivers a specific capacity of 120 $mC/cm^2\mu m$.

Conclusions: Lithiated transition metal oxides such as $LiCoO_2$ and $LiMn_2O_4$ thin films were deposited by pulsed laser deposition technique. The films deposited in an oxygen partial pressure of 100 mTorr and at a substrate temperature of 300 ^{o} C were found to be nearly stoichiometric with good crystalline structure. The surface morphology of these films exhibited uniformly distributed roughly spherical grains. The electrochemical properties of these were tested by fabricating electrochemical cells with the grown films as cathode materials and Lithium as an anode. The cells with $LiCoO_2$ thin films as cathode delivered a specific capacity of 190 $mC/cm^2\mu m$ where as the cells with $LiMn_2O_4$ thin films delivered only 120 $mC/cm^2\mu m$. The results suggest that the pulsed lased deposition is an excellent method for the growth of lithiated transition metal oxide thin films with a promising application in the fabrication of all solid state thin film microbatteries.

References:

1. J.B.Bates, N.J.Dudney, B.Neudecker, A.Ueda, C.D.Evans, Solid State Ionics, 135(2000)33
2. C.Julien, H.E.Parriatovski, O.M.Hussain and C.V.Ramana, Ionics, 7(2001)165
3. J.C.Miller and R.F.Haglmel , Laser Ablation and Deposition, Academic Press, New York,1998
4. K.A.Striebel, C.Z.Deng, S.J.Wen and E.J.Cairns, J.Electrochem.Soc., 143(1996)1821
5. D.Singh, W.S.Kim, V.Cracium, H.Hofmann, R.K.Singh, Applied Surface Science, 197(2002)516.

Preparation of Pure and Al-; Ga-; In-Doped ZnO Thin Films by Pulsed Laser Deposition and Radio Frequency Sputtering and Their Characterization – An Overview

V. N. Mani

Centre for Materials for Electronics Technology (C-MET),
Cherlapalli, Hyderabad 500 051
Email: vnm_crystal272001@yahoo.com

Abstract

The results highlighted in this talk pertain to the pure and Al-, Ga- and In-doped ZnO thin films growth by pulsed laser deposition (PLD), radio frequency (RF) sputtering and their structural, optical, electrical and surface characterization. The focused research methodology, which was adopted during the study, is as follows: Initially a batch of pure and Al-, Ga-, In-doped ZnO samples have been prepared and their properties were studied. After ascertaining the property improvement with respect to the varied and modified experimental conditions and parameters, further optimized deposition cycles have been carried out. A series of pure and Al-, Ga-, In-doped ZnO thin films on glass and silicon substrates have been grown by the PLD and pure ZnO thin films were also deposited by RF sputtering. Gallium of 5N+ purity, aluminum and indium of 4N purity were used for depositing of doped ZnO films. The effect of various experimental conditions and parameters such as laser and r.f. power, substrate temperature, deposition time, partial pressure of gases on the structural, optical, electrical properties of the ZnO thin films have been studied. X-Ray diffraction (XRD), atomic force microscopy (AFM), UV-Vis-NIR spectroscopy, hall measurement system were used to characterize the ZnO films. To conclude, growth parameters and heat treatment influence the structural homogeneity and surface properties of the ZnO thin films. The results on the crystalline quality and surface morphology of the pure and doped ZnO films vis-à-vis deposition conditions and parameters are interpreted**.**

Bandwidth control effects in electron doped manganite $La_{0.7-x}Y_xCe_{0.3}MnO_3$

K. P. Bajaj[#], P. Raychaudhuri[*], John J[*]and V. Bagwe[*]
Dept.of physics,Mumbai University,Mumbai-400089.
#Email: bajajkp@rediffmail.com
*Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Homi Bhabha Rd., Colaba, Mumbai 400005.

Abstract

We report on the effect of average A site cation radius on the structural, magnetic & electrical properties of electron doped manganite $La_{0.7}Ce_{0.3}MnO3$ thin films. A site cation radius $\langle r_A \rangle$ is varied systematically by replacing La^{+3} ions by smaller Y^{+3} ions in the parent compound. The carrier doping, i.e. the fraction of tetravalent Ce atoms at the A-site was kept at 30%. A series of $La_{0.7-x}Y_xCe_{0.3}MnO_3$ (x=0,0.05,0.1,0.15,0.25) thin films were prepared under identical conditions by using pulsed laser deposition technique. Metal insulator transition temperature (T_p) & Ferromagnetic Curie temperature (T_c) are found to be decreasing significantly with increasing yttrium concentration i.e decreasing $\langle r_A \rangle$. Amplitude of resistivity increases by one order of magnitude, while Spontaneous magnetization decreases with decreasing $\langle r_A \rangle$. Magnetoresistance as measured under field of 1Tesla is significant near T_c. Structural analysis reveals the films are having single phase & c-axis lattice parameter decreasing linearly from 7.7895 A^o to 7.7406 A^o as $\langle r_A \rangle$ decreases from 1.294 nm for parent compound to 1.25 nm for the highest doped sample. The decrease in $\langle r_A \rangle$(lattice distortion) results in decrease in Mn-O-Mn bond angle which in turn reduces the matrix element of electron hopping between Mn^{+2} and Mn^{+3} and reduces the carrier bandwidth of e_g band. Thus we have studied the evolution of magnetotransport properties of electron doped manganite by controlling Bandwidth.

Electrochemical Properties of Pulsed Laser Deposited TiO_2 – Doped $LiCoO_2$ Thin Films

M. C. Rao and O.M.Hussain*
Thin Film Laboratory, Department of Physics, Sri Venkateswara University,
TIRUPATI – 517 502, India.
*Email: hussainom48@yahoo.co.in

Abstract

$LiCoO_2$, one among the transition metal oxides has received significant attention in the fabrication of rechargeable lithium ion batteries because of its high theoretical specific capacity, energy density and high cycling stability. The deposition of $LiCoO_2$ in thin film form is of great interest because of their possible use as positive electrode in all solid state microbatteries to power microelectronics. Hence in the present investigation Ti-doped $LiCoO_2$ thin films were grown by pulsed laser deposition technique. The influence of deposition parameters on the growth and electrochemical properties of Ti-doped $LiCoO_2$ thin films were studied. Li//$LiTi_yCo_{1-y}O_2$ cells were tested in the potential range 2.6-4.2 V. Specific capacity as high as 225 $mC/cm^2\mu m$ was measured. These results suggest that the Ti-doped $LiCoO_2$ PLD films find potential applications as binder free electrode in the fabrication of all solid state microbatteries.

LD-2005: Posters – P 3

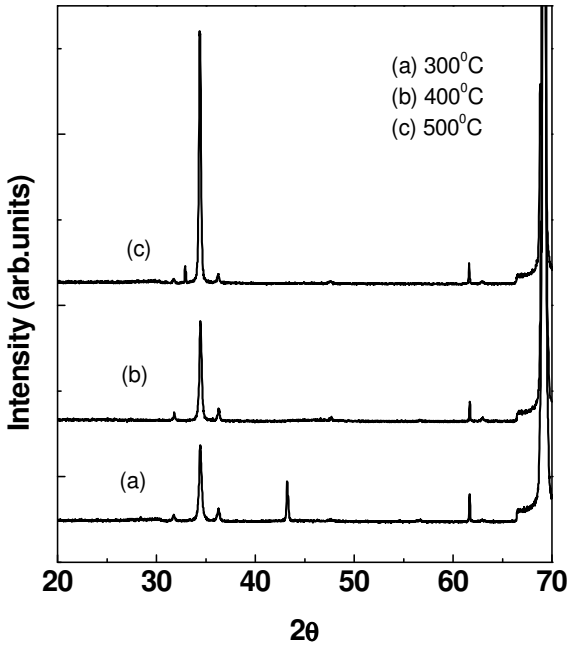
Structural and electrical behavior of Mg doped ZnO thin films grown by pulsed laser ablation

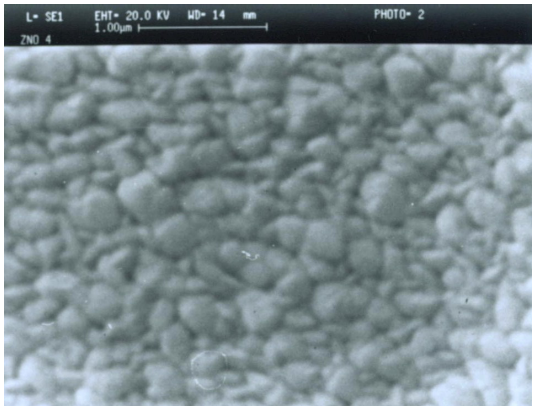
Dhananjaỹand Nagaraju J.
Department Of Instrumentation, Indian Institute Of Science, Bangalore 560012, India
Palash Roy Choudhury and S.B.Krupanidhi
Email: dhaya@isu.iisc.ernet.in

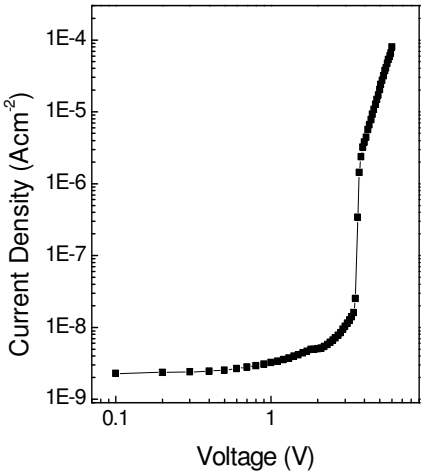
Materials Research Center, Indian Institute Of Science, Bangalore, 560012, India

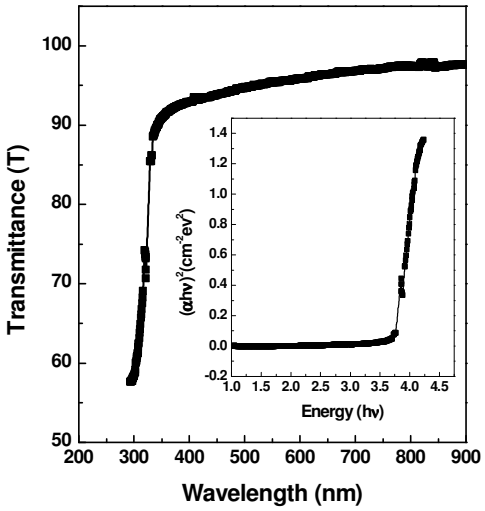
Abstract

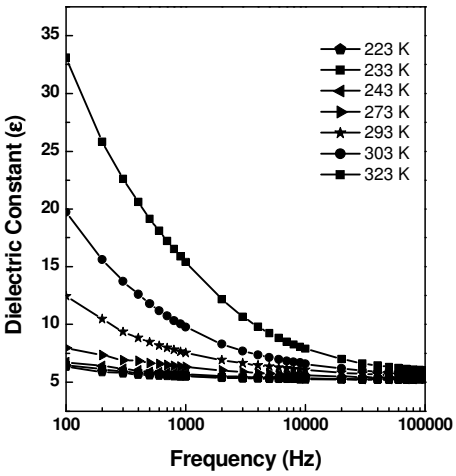
Mg doped ZnO thin films were grown on various substrates like (100) oriented Si and corning glass by pulsed laser deposition (PLD) technique. Highly c-axis oriented films were grown at a substrate temperature of 500^0C and 100mTorr oxygen ambient. The films were highly resistive and possess a compact nodular surface morphology with a columnar structure in cross-section. Both dc and ac transport properties of the films were carried out in order to reveal the conduction mechanism in these films. The current-voltage characteristics of these films indicated an ohmic behavior in the low voltage region, while higher voltages induced bulk space charge. Dielectric response of these films deposited by PLD has been studied as a function of frequency over a wide range of temperature. The films exhibited frequency dispersion in both real and imaginary part of the dielectric constant and could be attributed to the space charge effect. It has been observed that the incorporation of Mg into the ZnO lattice enhances the dielectric constant. The average transmittance of the films was higher than 90% in the wavelength range 400-900nm. The band gap was enhanced to 3.7eV with 20%Mg doping into the ZnO lattice making the band gap engineering feasible.

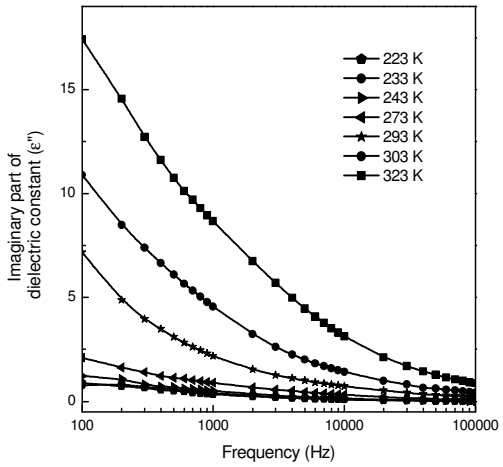

(a) 300^{0}C
(b) 400^{0}C
(c) 500^{0}C
(c)
(b)
(a)
Intensity (arb.units)
20
30
40
50
60
70
2θ


L- SE1
EHT- 20.0 KV
WD- 14 mm
1.00μm
PHOTO- 2
ZNO 4









References:

1. K.Matsubara, H.Tampo, H.Shibata, A.Yamada, P.Fons, K.Iwata, and S.Niki, Appl.Phys.Lett. 85 (2004) 1374
2. S.Choopun, R.D.Vispute, W.Yang, R.P.Sharma, and T.Venkatesan, Appl.Phys.Lett. 80 (2002) 1529
3. T.Minemoto, T.Negami, S.Nishiwaki, H.Takakura, and Y.Hamakawa, Thin Solid Films 372 (2000) 173

Bright Luminescence from Gadolinium doped Silicon nanoparticles prepared by off axis Pulsed Laser Deposition

J.R.Rani*, and V.P.Mahadevan Pillai
Department of Optoelectronics, University of Kerala, Thiruvananthapuram,Kerala, India - 695581
*Email: ranijnair @rediffmail.com

Abstract

Silicon , which is the backbone of microelectronic industry is not widely used for optoelectronic industry because of its indirect band gap . But silicon nanostructures having a quantum confinement effect have provided a breakthrough to optoelectronic applications because the quantum confinement effect enhances the electron-hole radiative recombination rate[1] .Rare earth doping of silicon based compounds has been the subject of intensive research because of its potential to combine sharp , temperature stable rare earth luminescence with the convenience of electrical excitation . The approach of introducing Gd ions in to Silicon networks is a very promising alternative for using Silicon in Optoelectronic industry . The distinctive energy level diagram of Gd3+ ions is motivating the perspectives of a new compound for photonic applications . As a Light-emitting devices made of silicon-based materials can be integrated into the existing microelectronic and optoelectronic technologies in a highly economic way; therefore enormous efforts have been devoted to the development of silicon-based structures that promise efficient light emission in the past decade[2]. From the point of view of optoelectronic applications , such devices should offer tunable light emission with utilizable efficiency in the whole visible light range or at even shorter wavelengths.

In this paper we report the pulsed laser deposition of Gadolinium doped Si nanoparticles at room temperature . The deposition was carried out by keeping the substrate in the off axis configuration . Gadolinium doped Si pellets were used as the target material and fused quartz as the substrate. A Q - switched frequency doubled Nd: YAG laser (fluence of $4x\ 10^{-6}$ J/m^2 at 532 nm, 9 ns pulse width, 10Hz repetition frequency) was used to ablate the target . The Gadolinium concentration used as 1at%.The Target was rotated with constant speed to ensure uniform ablation .The substrates were kept at target to substrate distance 5mm and 3cm off axis with respect to laser plume

Deposition chamber was initially evacuated to a base pressure of $5x10^{-6}$mbar and deposition was done at room temperature. Optical absorption spectra were recorded using a UV-VIS-NIR spectrophotometer (Hitachi U 3410) in the spectral range of 200 – 800 nm. The band gaps were determined from the plot ($\alpha h\nu$)^m verses $h\nu$ and by extrapolating the linear position near the onset of absorption to the energy axis [3-4] . Photoluminescence spectra of erbium doped Silicon nanoparticles specimens have been measured and analyzed to extract spectral contributions due to quantum confinement effects . The PL measurements were recorded by JobinYvon Spectro flurometer (Flurolog III) . PL emission wavelength varies between 375 and 550nm depending upon the excitation wavelength . PL results shows that luminescence does not originate from localized states in gap but from extended states.

The nano structure of films was examined by a HITACHI H – 600 TEM operated at 75 KV.. The transmission electron microscope image clearly shows that Si quantum dots are well organized in the silicon matrix and the average grains size is around 1.5 nm.

[1] Takagi H, Ogawa H, Yamazaki Y, Ishizaki A and Nakagiri T 1990 *Appl. Phys. Lett.* **56** 2379
[3] Baru V G, Chernushich A P, Lauzanov V A, Stepanov G V,Zakharov L Yu, O'Donnell K P, Bradley I V and Melnik N N 1996 *Appl. Phys. Lett.* **69** 4143
[4]A.Goswami, Thin film Fundamentals, New Age International (p) Limited (1996)
[5] Pankove J I, Optical *processes in semiconductors,* New Jersey, USA, 1971, p. 34

Characterization of Pulsed Laser Deposited Tungsten Trioxide (WO_3) Thin films

K.J. Lethy*, J.R.Rani, D.Beena, R.Vinodkumar, K.G. Gopchandran &V.P.Mahadevan Pillai
Department of Optoelectronics,University of Kerala, Thiruvananthapuram,Kerala, India -695 581
*Email: lethykj@yahoo.co.in

Abstract

Tungsten trioxide (WO_3) thin films are of great technological interest as transparent conducting electrodes and hold a central role in the emerging field of optical switching devices[1, 2]. WO_3 is an n-type transition metal oxide semiconductor which is a representative of a group of materials known as chromogenics. It displays both electrochromism -change of colour with an applied electric field, and photochromism –the change in colour under illumination. Moreover WO_3 is a widely used gas detector to detect toxic gases like CO, H_2S, and NO_x in domestic, commercial and industrial applications[3].

Thin films of tungsten oxide were deposited on fused quartz (silica) substrates using pulsed laser deposition technique. A Q-switched Nd: YAG laser (Quanta-Ray INDI – series, Spectra Physics) with a wavelength of 532 nm, pulse width 8 ns, repetition rate of 10 Hz, and maximum output energy 250 mJ was used to ablate the WO_3 target. Commercial WO_3 powder of 99.995% purity was used to make pressed target (11 mm in diameter and 4 mm thickness). The target was rotated uniformly during deposition to avoid depletion of material at any given spot and to obtain uniform thin films. The deposition chamber was evacuated to a base pressure of $4x10^{-6}$ mbar using a diffusion pump and a rotary pump. Thin films were grown in a non-reactive atmosphere at room temperature. Thin films were deposited by both on-axis (substrate to target distance 7.5 cm) and off-axis (substrate to target distance 3 cm) laser deposition method. The deposition time was 15 minutes and the energy of the laser beam was maintained at 93 mJ during deposition. The as deposited films (both on-axis and off-axis) were metallic in appearance. It has been reported by J.G Zhuang *et.al* that WO_{3-y} films have a metallic aspect for y>0.5 and are conductors [4]. Films were annealed at two different temperatures 623K & 773K for 3 hours in air.

X-ray diffraction (XRD) measurements were carried out to study the crystalline properties of the prepared (as-deposited and annealed at 623K &773K) WO_3 films. The XRD pattern was recorded using CuKα- radiation of wavelength (1.54056 A^o). Study of x-ray diffraction pattern of films reveals that as-deposited films are amorphous while the films heat-treated at 773K for 3 hours in air crystallize to WO_3. The average grain size of the crystallites were estimated to be about 30 nm by using Scherrer's formula [5]. Effect of post -annealing on crystallization and grain size was also studied.

Optical transmittance (T) and reflectance (R) were measured by spectrophotometry in the wavelength range 200-800 nm. The quartz substrates used are transparent in this range. Measurements were carried out using UV-VIS-NIR Spectrophotometer (Hitachi U 3410). The transmittance of the as - deposited films were nearly 50%. From the absorbance spectra band gap energy of the as deposited films were estimated to be about 3.8eV and it shows a blue shift in band gap energy compared with the band gap energy of bulk sample which is about 3.25 eV. The impact of heat-treatment on percentage transmittance and band gap energy were also examined.

Only a few reports were available on the photoluminescence properties of tungsten trioxide thin films[6, 7]. Photoluminescence spectra of the films were recorded using Jobin Yvon Fluorolog-III (450 W Xe arc-lamp,excitation at 260 nm) Spectroflurometer. These laser ablated films exhibit strong PL emission at 404 nm. Variation of photoluminescence emission with annealing was also studied. The surface morphology and the crystalline grain size of the grown films were investigated using Transmission Electron Microscopy (HITACHI H-600 TEM) operating at 75 kV.

References

[1] Hiroharu Hawasaki, Jun Namba, Keitarou Iwatsuji , *Appl.Surf.Sci*. **197 -198** (2002) 547-551

[2] Robert G.Palgrave, Ivan P Parkin, *J.Mater.Chem.* 2004, **14,** 2864-2867

[3]W.Gopel, K.D Schierbaum , *Sens. Actuators B* 26-27 (1995) **1**

[4] J.G Zhuang, D.K benson, C.E Tracy, S.K Deb, A.W Czanderna, C.Bechinger, *J.Electrochem.Soc.* 144 **(6)** (1997) 2022

[5] B.D Cullity, *Elements of X-ray Diffraction* (Addison-Wesley, Reading, MA,1959)

[6] Kwangyeol Lee, Won Seok Seo, and Joon T. Park, *J.AM.CHEM.SOC*.2003, **125**,3408-3409

[7] Feng. M , Pan A.L, Zhang H.R, Li . Z .A, *Appl.Phys.Lett*. **86** (14) 2005

AC conduction studies of pulsed laser ablated multiferroic $BiFeO_3$ thin film

Somenath Bose[♣] and S.B.Krupanidhi
Materials Research Centre, Indian Institute of Science, Bangalore-560 012
*Email: bose@mrc.iisc.ernet.in

Abstract

Magnetoelectric materials, in which both magnetic and electric ordering exists, has generated increasing interest in recent times due to their application potential in different devices, e.g. sensors, memories, actuators etc [1]. Bismuth ferrite (BFO) is a magnetoelectric multiferroic material in which both ferroelectricity and anti-ferromagnetism exists at room temperature. In the present work $BiFeO_3$ (BFO) thin films were deposited from sintered target of $BiFeO_3$ by pulsed laser deposition technique. BFO films were deposited at 675°C at 50mTorr oxygen pressure. Laser pulse frequency was 5 Hz and fluence 4 J/cm^2 (approx.) during deposition. Polycrystalline nature of as-deposited films was verified by x-ray diffraction pattern in a scintag xrd-instrument. BFO films obtained show a preferential orientation along (110) direction with low intensity (012) and (024) peaks. Gold dots were deposited on top of as-deposited films by thermal evaporation for electrical characterization. Ferroelectric hysteresis (fig.1) measured in a RT-66A loop tracer confirms the ferroelectric nature of BFO films. A maximum polarization of 4.2 μC/cm^2 was obtained at a field of 81.7 kV/cm, which is comparable to other studies on polycrystalline BFO films [2]. Saturated hysteresis loop could not be obtained due to leaky nature of the sample. Magnetic hysteresis was measured in a lakeshore vibrating sample magnetometer and shows the ferromagnetic nature (fig.2) of the sample. Saturation magnetization attained (1.75 emu/cm^3) is very small as compared to magnetic ferrite thin films. This unexpected ferromagnetic nature in thin film form is explained by the canting of spins of Fe atoms. DC and AC transport studies were performed on BFO thin films to find out the exact nature of electrical conduction and dielectric relaxation mechanism respectively. Leakage current density increases very fast with increase in temperature. AC impedance analysis shows that the material response is non-Debye type with distribution of relaxation times. Only one semicircle (fig.3) was obtained in the complex impedance plane plot (Z'-Z''). This is believed to arise from the grain; grain boundary or electrode response was not observed in the frequency (100Hz-100kHz) window of the experiment. AC conductivity of the material increases with frequency (fig.4) at low temperatures and obeys Jonscher's power law [3] relationship. A frequency independent plateau in ac conductivity was observed at high temperatures, which shifts towards high frequency side with increase in temperature. At temperatures higher than 200°C ac conductivity becomes almost frequency independent, this was due to dc conduction, which is frequency independent. AC conductivity shows Arrhenius type behavior with temperature (fig.5) with two distinct activation energies, which can be attributed to two different conduction mechanisms. At low temperatures activation energy varies between (0.07 to 0.13eV) for different frequencies and is expected to arise from hopping conduction between defect states. At high temperatures the activation energy increases to 0.9 to 1.1eV, which is very common in ferroelectric oxide thin films [4] and arises due to oxygen vacancy conduction. A further confirmation of the oxygen vacancy transport was obtained from DC studies, where the dc conductivity v/s reciprocal temperature plot also gives activation energy in the same range (0.85-1.15eV).

[♣] Contact author email id: bose@mrc.iisc.ernet.in

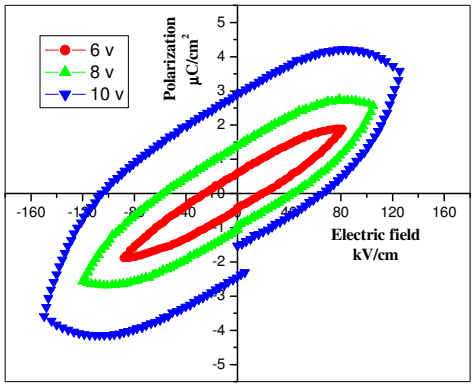


Fig1. Ferroelectric hysteresis loop of BFO thin film at room temperature.

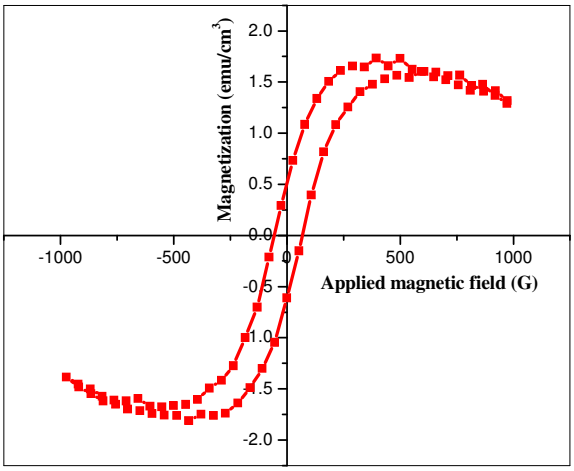


Fig2. Ferromagnetic hysteresis loop of BFO thin film at room temperature.

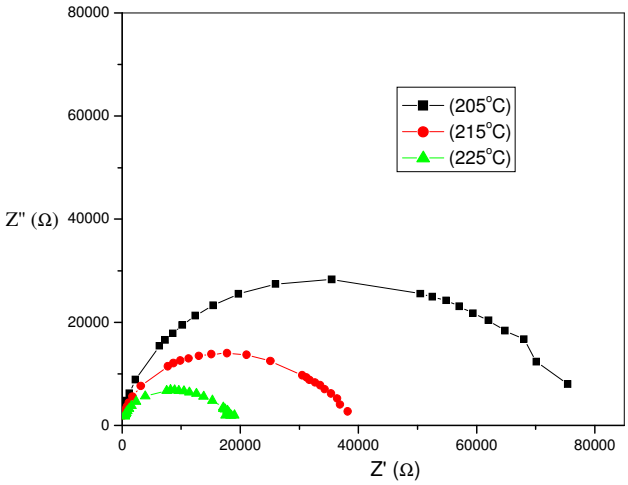


Fig.3. Complex impedance plane plots at different temperatures.

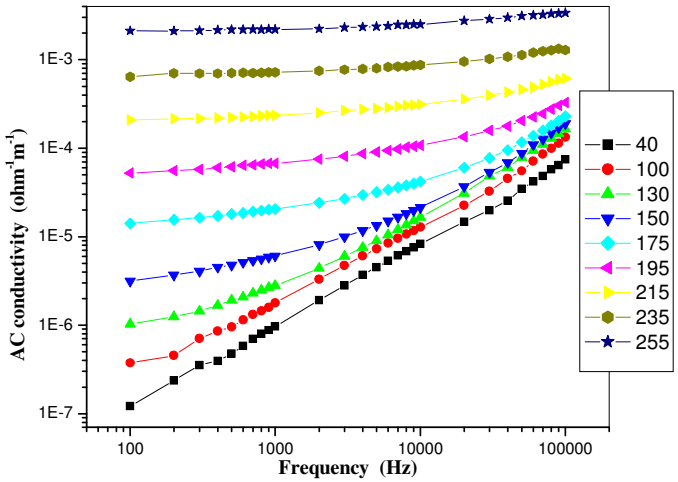


Fig.4. AC conductivity with frequency at different temperatures.

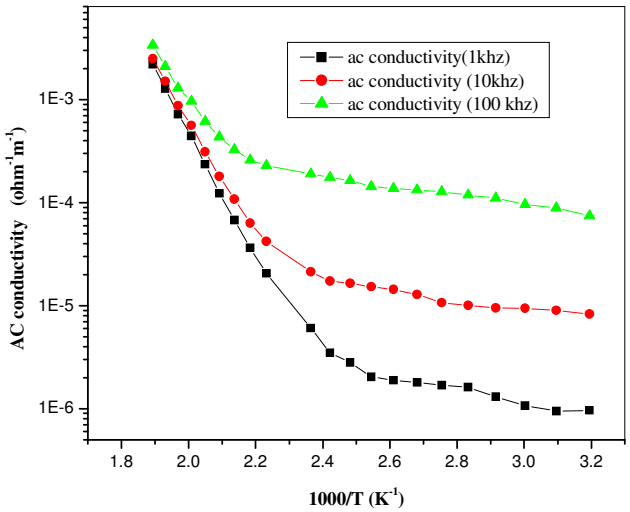


Fig.5. Arrhenius type behaviour of ac conductivity.

Major References:

1. J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithylyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spal-din, K. M. Rabe, M. Wuttig, and R. Ramesh, Science **29**9,1719 (2003).
2. V. R. Palkar, J. John, and R. Pinto, Appl. Phys. Lett. 80, 1628 (2002).
3. A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics, London, 1983).
4. S. Saha and S. B. Krupanidhi, J. Appl. Phys. **8**7,849 (2000).

Pulsed Laser Deposition of Magnetite thin films

Murtaza Bohra[1], Naresh Kumar[1], D. S. Misra[1], N.Venkataramani[2] and Shiva Prasad[1]
[1]Physics Department, [2] Department of Metallurgical Engineering and Material Science[2], Indian Institute of Technology Bombay Powai, Mumbai 400076,

Abstract

INTRODUCTION

Pulsed laser deposition (PLD) has been shown to be very successful method for growth of materials in thin film from both as epitaxial layers and as amorphous films. Few of the characteristics feature of PLD are, stoichiometric transfer, and growth from an energetic beam, reactive deposition, and simplicity of operation.[1] Recently Fe_3O_4 films have received a lot of attention due to combination of several interesting properties. They are half metallic as per band-structure calculations[2]. They also have high Curie temperature (T_c) of 858K and a weak magneto-crystalline anisotropy. Hence they are being looked as future spintronic materials.

We have deposited Fe_3O_4 thin film by PLD from Fe_3O_4 and α-Fe_2O_3 targets. In this brief report, we will discuss the magnetic, electrical, and crystalline properties of Fe_3O_4 film deposited by PLD from α-Fe_2O_3 target on to fused quartz substrate.

EXPERIMENTAL DETAILS

The Fe_3O_4 thin films were grown on fused quartz substrates by PLD using Q switched Nd:YAG laser (λ=355 nm, pulsed width 5 ns and 10 Hz repetition rate) from α-Fe_2O_3 target. The typical fluence of the focused laser beam on the target was 2.5 J/cm^2. The substrates were kept at a distance 3.5 cm from the target and heated in situ to 350°C during deposition. The chamber was evacuated to a base vacuum of 5.4×10^{-6} mbar and during the deposition vacuum of 1×10^{-5} mbar was maintained. The as deposited film was also annealed in wet H_2 atmosphere at 450°C for 15 min. The crystal structures of the films were studied by x-ray diffraction (XRD). The M_S was measured at RT using a vibrating sample magnetometer (VSM). Resistivity (ρ) of the films was measured by four-probe method in range of 50 K to RT and the magneto -resistance (MR) at RT in a field of 2.4T.

RESULTS AND DISSCUSTION

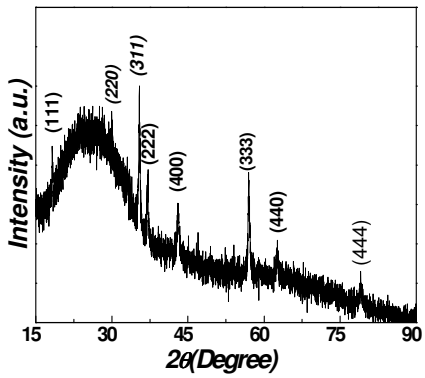


Figure1. XRD patterns for Fe_3O_4 film.

Figure 1 shows the X-ray diffraction pattern of the Fe_3O_4 film. The lattice constant a = 0.8392 nm is close .to the JCPDS (card no.19-0629) value of cubic Fe_3O_4 bulk powder.

γ -Fe_2O_3 has a similar crystal structure to that of Fe_3O_4 with a lower magnetization value. Hence the film has been characterized using x-ray photoelectron spectroscopy (XPS). It is well established that the satellite peaks in the XPS spectroscopy can help to identify the chemical states of iron in its oxides.[3] One remarkable difference between the γ-Fe_2O_3 and the Fe_3O_4 is that the former has satellites in the Fe 2*p* core level spectra while the latter does not have this satellite feature. Figure 2 shows the Fe 2*p* core-level spectroscopy of the film, obtained with normal emission using Mg-*K* a radiation, which agrees well with the reported Fe_3O_4 spectra.[3] The broad Fe-2*p* peaks are attributed to the coexistence of Fe^{3+} and Fe^{2+} states, and at the same time, no satellites could be identified around the binding energy of 719 eV. This excludes the possible presence of γ-Fe_2O_3 in our film.

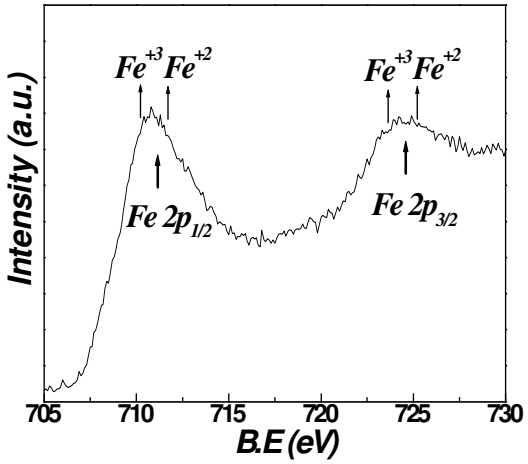


Figure2. Fe 2*p* core-level XPS spectra for Fe_3O_4 film.

The value of saturation magnetization ($4\pi M_s$) of the Fe_3O_4 film is 5370 G, which is 91% of the bulk value of 5900G and the coercive field is about 320 Oe. The lower magnetization value for the film is in keeping with several reported observations in the case of thin film materials.

The room temperature resistivity (ρ) values for Fe_3O_4 film was found to be ~90 mΩcm. In Fig.3, the four-probe resistance was recorded as a function of temperature. The Arrhenius plot (ln ρ vs 1/*T* in the inset) shows a linear relation, suggesting a thermally activated hopping transport mechanism. An activation energy of E_a ~ 76 meV was estimated by fitting the curve using $\rho = \rho_0 \exp(E_a/k_BT)$. Also noteworthy is the absence of Verwey transition in these films, which has also been observed in polycrystalline Fe_3O_4 films[4]. It was suggested that in a system with high resistivity and small grain size, the linear hopping chain lengths are shortened[5] and thus preventing the occurrence of Verwey transititon.

The magnetoresistance, MR = 1− (R_H/R_0) for a resistance R_H in a magnetic field H and the maximum value R_0 for the Fe_3O_4 film measured by applying the magnetic field of 2.4 T.

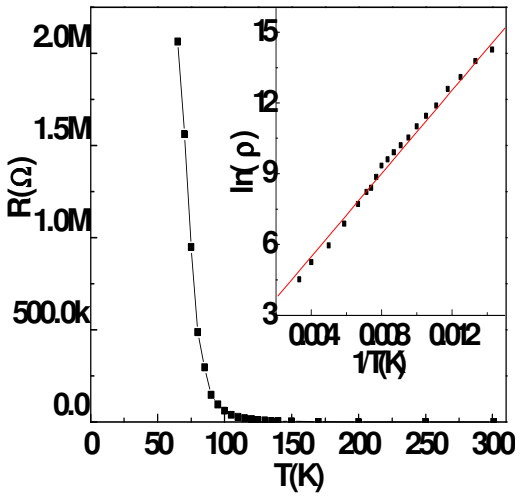


Figure3. Resistance (R) vs temperature (T) curve. (Inset) lnρ plotted as a function of 1/T.

The MR was measured in transverse geometry, with the current perpendicular to the magnetic field. A negative MR of 2.1 % was observed for the films at room temperature in a magnetic field of 2.2 T. The negative MR in such thin films has been described to occur though a spin dependent tunneling in the network of contiguous grains[5].

Conclusion: We have deposited Fe_3O_4 thin films with magnetization value close to the bulk, from Fe_2O_3 target, on quartz substrates using PLD. XPS data correlates the presence of single phase Fe_3O_4 inferred from the XRD observation. A room-temperature MR of ~2.1 % was also observed.

References

1. W. M. K. P. Wijekoon and M. Y. M. Appl. Phys. Lett. 67, 1698 (1995).
2. Yanase and K. Siratori, J. Phys. Soc. Jpn. 53, 312 (1984).
3. Ruby, B. Humbert, and J. Fusy, Surf. Interface Anal. 29, 377 (2000).
4. Hui Liu, E.Y.Jing and X.X.Zhang Appl. Phys. Lett**.** 83, 3531 (2005).
5. W. Eerenstein, and S. Celotto, Phys. Rev. B 66, 20110(R) (2002).

Physical properties of doped ZnO thin films grown by Pulsed Laser Deposition

Shubra Singh, N Rama, M.S.Ramachandra Rao

Department of Physics and Material Science Research Centre,

Indian Institute of Technology (IIT) Madras, Chennai - 600 036.

Abstract

Pulsed laser Deposition (PLD) has been found to be a very viable technique for the deposition of diluted magnetic semiconductor (DMS) thin films due to its versatility, simplicity, and control of stoichiometry. Recent trends in this area have emphasized its unique properties and have made it a prime thin film growth tool for growing highly crystalline compound semiconductor epitaxial layers. The purpose of this paper is to evaluate the physical properties of rare-earth (RE) and transition metal (TM) ion doped ZnO thin films grown by PLD. The recent spur of activity that promoted ZnO as a promising DMS (diluted magnetic semiconductor) host, compared to Mn-doped GaAs, with metal ion doping [1] has prompted us to undertake the work reported in this abstract. ZnO can be grown into large-scale, high-quality single crystalline thin-films and ZnO is a potential host for rare-earth (RE) ion doping [2].

In a search for new methods for growing diluted magnetic semiconductors (DMS), we have made an attempt to make $Zn_{1-x}Dy_xO$ and its structural and magnetic properties were studied. Role of ZnO as DMS host has also been explored by doping it with a transition metal ion like Ni and the electrical, optical as well as magnetic properties were studied. The bulk as well as thin film resistivity was found to decrease remarkably with small concentrations ($0.0 < x < 0.3$ mol%) of Ni which definitely makes, if magnetism is found, it a transparent ferromagnet that can offer interesting magneto-optic applications.

Key words: PLD, ZnO, Thin films

[1]. J. M. D. Coey et al. Appl. Phys. Lett. **84**, 1332 (2004).

[2] W.M. Jadwisienczak et al. Journal of Electronic Materials, **31**,776-784,s (2002).

Deposition of silicon nitride films by DC discharge aided pulsed laser deposition

Ram Prakash [*] ***and D.M.Phase***

UGC-DAE Consortium for Scientific Research, Khandwa Road, University Campus, Indore-452 017.

*Email : ramprakash@csr.ernet.in

Abstract

Silicon nitride is one of the most interesting thin film materials in the semiconductor device technology. The outstanding advantages of thin films in the silicon-nitrogen system are the tailorable electronic and optical properties, which are highly dependent on the chemical composition. There are some reports on the fabrication of silicon nitride films by Pulsed Laser Ablation (PLA) technique in ammonia gas. Preparation of the silicon nitride film from a Si target and nitrogen gas thought to be difficult since nitrogen gas is stable. In this paper we report a synthesis of silicon nitride films by DC discharge aided reactive pulsed laser deposition (PLD). The PLD was performed in a custom made high vacuum chamber. This PLD chamber is modified and two planer circular (7cm dia.) electrodes were fitted above and below the target assembly. DC supply of 500V was connected to generate the discharge. The ablation energy source was a KrF excimer laser of λ = 248 nm. The beam was focused down to a size of ~ 2 x 1 mm^2, onto the surface of a target. A high purity single crystal silicon wafer was used for the target and substrate. The distance between target and substrate was 40 mm. The target was rotated at 5 rev/min.. Silicon nitride films were synthesized at room temperature by means of laser ablation of a silicon target with and without DC discharge in pure nitrogen gas. Deposited films were characterized by using Scanning electron microscopy with EDX analysis, Atomic force microscopy and x-ray photoelectron spectroscopy. The film deposited with and without DC discharge show drastically different behavior. It is found that DC discharge aided films show higher and uniform nitrogen content than that of film deposited without DC discharge. Our results indicate that presence of the DC discharge during the deposition lead to enhance nitridation of the ablated silicon.

PLD grown nanostructured n-Carbon/p-Si thin film interfaces

K. Mohan Kant[1,2,*], K.Sethupathi[2], and M.S. Ramachandra Rao [1,2]

[1]Materials Science Research Centre, Indian Institute of Technology Madras, Chennai.
[2]Department of Physics, Indian Institute of Technology Madras, Chennai.
*Email: mohankant@physics.iitm.ac.in

Abstract

Nanostructured carbon thin films are of great interest due to their potential device applications. Carbon films interfaced with (n or p type) Si substrates which show non linear I-V characteristics have potential application in field-emission devices (FEDs) [1]. We have studied the effect of growth parameters on the physical properties of PLD grown carbon films using a graphite target at different Ar-partial pressures. Atomic force microscopy (AFM) studies showed that the grain size is about 80-90 nm. Substructures were seen in the thin films grown for higher deposition time (~ 30 min) corresponding to a thickness of 300 nm. With decrease in deposition time, grain size was found to decrease correspondingly. All the films showed semiconducting behaviour. The conduction mechanism was found to be 3D Variable Range Hopping (VRH) mechanism. Carbon films were found to be n-type (n-C). We have deposited n-C films on p-Si substrates to study the current-voltage (I-V) characteristics. It is interesting to note that the n-C/p-Si heterostructures showed non- linear current-voltage characteristics indicating the diode-like nature of the interface. Electroresistance (ER) measured on these junctions yielded 96% ER which is a very significant result. We are in the process of growing carbon films using metal catalyst to enhance the nanostructured growth suitable for field emission in conjunction with a top phosphor layer. All the above results will be presented and discussed in detailed.

Pulsed laser deposited $Ca_3MgSi_2O_8$:Ce phosphor thin films for near UV LED converted blue light emission

P.Thiyagarajan[1,2], M.Kottiasamy[2], M.S.Ramachandra Rao[1,2,*]

[1]*Department of Physics, Indian Institute of Technology Madras, Chennai - 600 036.*

[2]*Material Science Research Centre, IIT-M, Chennai - 600 036.*

*Email: msrrao@iitm.ac.in

Abstract

Thin film of $Ca_3MgSi_2O_8$:Ce phosphor have been deposited by Pulsed Laser deposition (PLD) thin film growh technique using Si as a substrate. Ce doping in $Ca_3MgSi_2O_8$ produces a violet-blue emission on excitation by UV and near UV regions[1]. To optimize the photoluminescent (PL) emission intensity, the concentration of the Ce dopant was varied from 1 mol% to 5 mol%. Ce doped $Ca_3MgSi_2O_8$ phosphor was prepared by carbothermal reduction method using the chemical ingredients viz., $CaCO_3$, $MgCO_3.4Mg(OH)_2.5H_2O$, SiO_2 and CeO_2 in a reducing atmosphere at an elevated temperature (1200º C). The powder was then pressed and sintered into a target for PLD growth. Thin films were grown on Si substrate at low substrate temperature ~ 700º C in an oxygen partial pressure of 0.32 mbar. The fluence of the laser power was kept at 2.2 Jcm^{-2} during the deposition. X- ray diffraction (XRD) studies confirmed the phase formation. SEM pictures were taken. Thin film photo-luminescent (PL) emission and excitation spectra of the Ce doped $Ca_3MgSi_2O_8$ are shown in the Figure. Details of thin film growth and PL spectra will be presented and discussed.

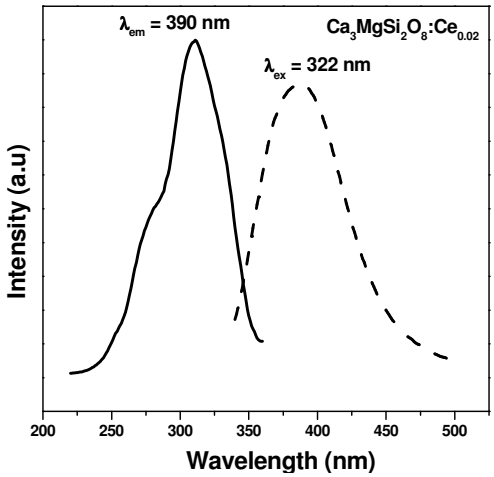


Fig. PL emission and excitation spectra of PLD grown $Ca_3MgSi_2O_8:Ce_{0.02}$ phosphor thin film

Reference

[1]. Huang Lihui, Zhang Xiao, Liu Xingren, J.All.Com. 305 (2000) 14-16

Effect of laser fluence on structure and properties of pulsed Nd/YAG laser deposited iron oxide thin films.

Shailja Tiwari, Ram Prakash, Atul Tiwari, U.P.Deshpande, T.Shripathi, D.M.Phase*

UGC-DAE Consortium for Scientific Research, Khandwa Road, University Campus, Indore-452 017.

email : dmphase@csr.ernet.in

and

Pankaj Misra and L.M.Kukreja

Thin Film Lab, Centre for Advanced Technology, Indore-452 013

Abstract

Magnetite (Fe_3O_4) is perhaps one of the most studied iron compound of the past 50 years because of its rather unique and interesting set of transport and magnetic properties. It has a cubic inverse spinel structure with tetrahedral sites occupied by Fe^{3+} ion and octahedral sites shared by Fe^{2+} and Fe^{3+} ions. The moments of the Fe^{3+} ion on octahedral sites are opposite to each other and the net moment arises only from the Fe^{2+} ion. The arrangement being termed as Ferrimagnetic. The presence of Fe^{2+} and Fe^{3+} ion on octahedral sites leads to a Fairly low electrical resistivity in this compound at room temperature. Due to carrier hopping between the $Fe^{2+}$and Fe^{3+}ion, it undergoes the Verway transition at 120K, below which it becomes a nonmagnetic insulator.

Pulsed laser deposition has been extensively used in obtaining thin films of magnetites from Fe_3O_4 or α-Fe_2O_3 target. The previous research has concentrated on the dependence of the structural and magnetic properties with oxygen flow rate and the substrate temperature. With increasing oxygen flow rate, the following sequence of phases has been reported: Fe, Fe_3O_4, and Fe_2O_3. In addition, granular composite films of Fe/ Fe_3O_4, Fe/$Fe_{1-x}O$ and Fe_3O_4/ Fe_2O_3 have been reported between the single-phase regions. The purpose of our present investigation is to consider the effect of laser fluence on the structural, compositional and magnetic behavior of Fe_3O_4 films. Magnetite thin films were prepared by pulsed laser ablation from α-Fe_2O_3 target on single crystal Strontium titanate (STO) substrate in a custom made high vacuum chamber. The ablation energy source was an Nd-YAG laser of λ = 355 nm. Laser fluence was varied from 1 J/cm^2 to 3 J/cm^2. The films were grown at a temperature of 600^{o}C in vacuum (~10^{-6} torr). Deposited films were characterized using x-ray diffraction, scanning electron microscopy, x-ray photoelectron spectroscopy and magneto optical Kerr effect (MOKE) technique. From obtained results an attempt have been made to correlate the effect of laser fluence on structure and properties of deposited thin films.

Studies on $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ Epitaxial Thin Films: An Application Point of View

J. H. Markna[1], R. N. Parmar[1], C. M. Thaker[1], P. S. Vachhani, J. A. Bhalodia[1], P. Misra[2], L. M. Kukreja[2], D. G. Kuberkar[1]

[1] Department of Physics, Saurashtra University, Rajkot-360 005, India
[2] Thin Film Lab., Centre for Advances Technology, Indore- 452 013, India

Abstract

$La_{1-X}A_XMnO_3$; A=Ca^{+2}, Sr^{+2}, Ba^{+2} etc. manganite having ABO_3 type perovskite structure has recently attracted much interest due to their potential application using the large magnetoresistance effect exhibited by them [1]. In this communication we report the results of the studies on magnetotransport properties of $La_{0.5}Pr_{0.2}Sr_{0.3}MnO_3$ (LPSMO) epitaxial thin films. Samples of LPSMO thin films with thickness 50 nm and 100 nm were grown by Pluses Laser Deposition (PLD) technique using the third harmonic (355 nm) of a Q-switched Nd: YAG laser having energy density of about 2.17 J/cm^2 at 10 Hz repetition rate. The films were deposited on chemically cleaned single crystal $SrTiO_3$ (*l00*) substrates. The structural studies using XRD revealed the epitaxial, single phase nature of LPSMO films having (*h 0 l*) orientation on STO substrate.

The magnetotransport measurement performed on the 50 nm and 100 nm LPSMO thin films at various temperatures under 0 to 9 Tesla applied magnetic field show that, both the films exhibits large magnetoresistance (MR % ~ 55 %) near the insulator to metal transition temperature (T_P) which can be primarily attributed to the large size disorder at A-site in LPSMO system. At low temperature, the films exhibit negligible MR, probably due to no grain boundary effect (Fig.1). To explore the half metallic nature of the films, unconventional one magnon scattering law $\rho(T) = \rho_0 + BT^n$ was fitted on to ρ – T data, in which ρ_0 is residual resistivity and B is electron – magnon scattering coefficient(not shown). The half metallicity is useful in understanding the spin valve mechanism in the manganites, which is originate from low field magnetoresistance and spin polarized current [2].

Field coefficient of resistance (FCR) defined as FCR = 1/R×dR/dT % Tesla $^{-1}$ is an important parameter from application point of view. In the present studies, it is observed that in the 50 nm LPSMO thin film, FCR value is 13 % in the 0.5 Tesla magnetic filed which is useful in the bolometric sensors. [3, 4]

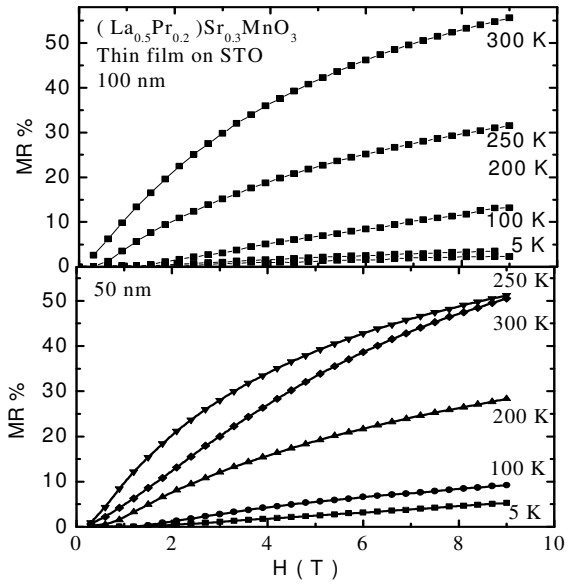


Figure 1 MR vs H(T) isotherms plots of LPSMO thin films(50 nm and 100 nm)

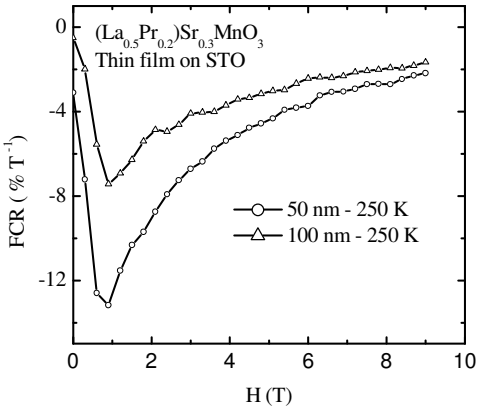


Figure 2 FCR vs H (T) plots of LPSM thin films (50 nm and 100 nm)

References:

1. Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, ed. by C. N. R. Rao, B. Reveau. (World Scientific Publishing Co. Pvt. Ltd. 1998).
2. T. Akimoto, Y. Moritomo, A. Nakamura and N. Kurukawa Phys. Rev. Lett. 85, 39149 (2000)
3. M. Rajeswari, A. Goyal, A. K. Raychaudhuri, M. C. Robson, G. C. Xiong, C. Kwon, R. Ramesh, R. L. Greene, T. Venkatesan, and S. Lakeou, Appl. Phys.Lett. 69 851(1996)
4. Ravi Bathe, K. P. Adhi , S. I. Patil, G. Marest, B. Honneyer, and S. B. Ogle, Appl.Phys.Lett. 76 2104 (2000)

Pulsed Laser Deposited Iso-Epitaxial WO_3 thin films for Gas Sensing Applications

A.S.Swapnasmitha[a], O.M.Hussain[a*] and R.Pinto[b]

[a]*Thin Film Laboratory, Department of Physics, Sri Venkateswara University, Tirupati-517 502*
[b]*Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, MUMBAI – 400 005, India*
*Email: hussainom48@yahoo.co.in

Abstract

The sensing of explosive, toxic and other pollutant gases has been the subject of research for more than two decades for monitoring the environmental pollution. Recently, transition metal oxide thin films are being used as gas sensors because of their suitable surface structure and good electrical properties. Tungsten oxide (WO_3) thin films with many interesting physical and chemical properties have been widely considered as good candidates for their use as environmental gas sensors for detecting pollutant gases like NO_x, NH_3, CO_x etc. Among these pollutant gases the nitrogen oxide NO_x (NO & NO_2) released from combustion facilities and automobiles have been one of the main causes of acid rain and photochemical smog. Also this can cause diseases of respiratory system of human beings. Hence the detection of nitrogen oxides are highly demanded to reduce the noxious effects on environment and human beings. In the case of environmental monitoring, the threshold limit value (TLV) for NO_2 is 3 ppm. Accordingly, an NO_2 sensor is required to have a high sensitivity than can correspond to such low TVLs. Thin films of WO_3 are considered to be one of the best candidates among NO_x sensing materials[1] due to its high sensitivity and good selectivity to low concentrations. Several thin film deposition techniques have been employed to prepare WO_3 thin films for their effective utilization in gas sensor applications. However the sensitivity, stability and repeatability towards a particular gas are mainly dependent on the surface structure and electrical properties of WO_3 thin films which inturn depend on the deposition technique and the process parameters. Recently, pulsed laser deposition technique has been widely recognized as a very promising, versatile and efficient method for the deposition of metal oxide thin films because of its reproducibility, controllability of stoichiometry and crystal structure. Another chief advantage is that pulsed laser deposited thin films crystallize at relatively lower deposition temperatures than the other physical vapor deposited films due to the high kinetic energy (>1eV) of the ionized species in the laser produced plasma[2] . Hence in the present investigation WO_3 thin films were prepared by reactive pulsed laser deposition technique. The influence of process parameters like oxygen partial pressure and substrate temperature on WO_3 thin films were studied. The NO_2 gas sensing properties of WO_3 thin films coated on $SrTiO_3$ substrates were also examined.

A KrF excimer laser (Luminics PM 882) with a wave length of 248 nm and a pulse duration of 30 ns delivered an energy of 300 mJ per pulse was used for ablation. The energy density of laser beam was 3 J/cm^2. The pulse repetition rate was set at 10 Hz. The distance between the target and the substrate was 4 cm. A sintered WO_3 target at 1073 K for 20 h was used for laser ablation The target was rotated at the rate of 10 rotations/min to avoid depletion of the material at the same spot during the deposition. The chamber was evacuated to a base pressure of

$2x10^{-6}$ Torr before the film deposition. During the deposition pure oxygen was introduced into the chamber and the desired pressure was maintained with a flow controller. The substrates were maintained in the temperature range 473 – 873 K and the oxygen partial pressure was maintained in range 100 – 200 mTorr. The thickness of the laser ablated WO_3 thin films was about 0.3 μm. The substrates used were (100) $SrTiO_3$ single crystal substrates.

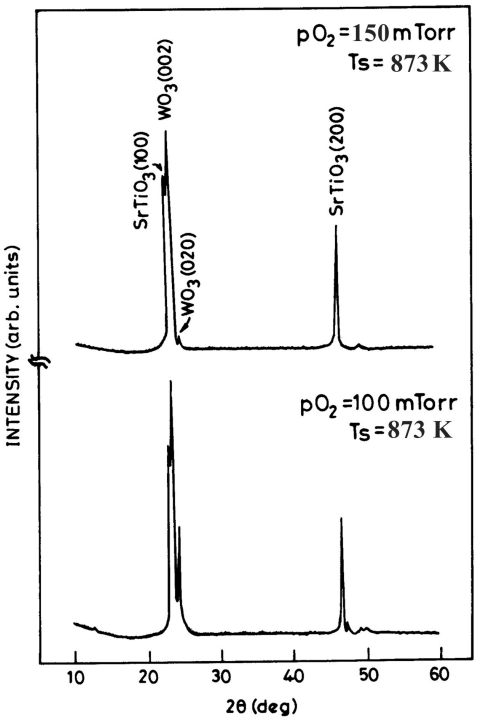


Fig. 1: The XRD spectra of $W0_3$ thin films deposited at 873K and at various oxygen partial pressures on (100) $SrTi0_3$

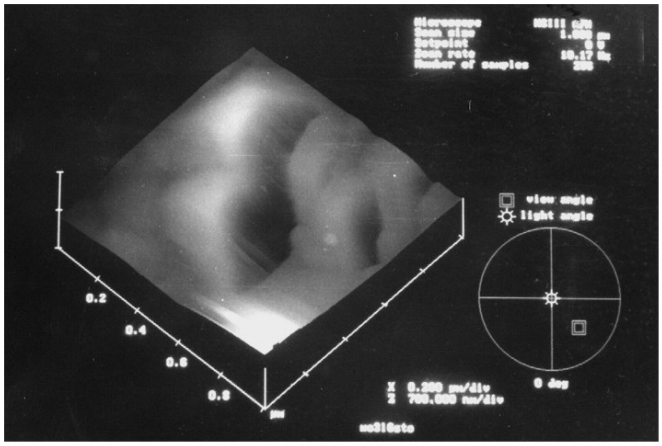


Fig. 2: Surface morphology of the $W0_3$ thin film deposited at a substrate temperature of 873K with an oxygen partial pressure of 150 mTorr.

en as an ideal substrate because it is a good elelctrical insulator having high thermal and structural stability at higher temperatures. Also it is having close lattice matching with WO_3 thin films. The reported 2θ positions for the (100) peak of $SrTiO_3$ and the (002) peak of WO_3 in bulk are 22.782 ^{0} and 23.118 ^{0} respectively[3]. $SrTiO_3$ possesses a cubic perovskite structure and its lattice constant is 3.905 Å. The laser ablated WO_3 thin films deposited on $SrTiO_3$ substrates are found to be well adherent to the substrate surface. A minimum oxygen partial pressure of 100 mTorr was maintained to grow transparent and stoichiometric WO_3 thin films. The WO_3 thin films deposited in the temperature range 473-873 K in an oxygen partial of 100 mTorr exhibited three peaks in the 2θ range 23-25 ^{0} with (002), (200) and (020) orientations. However all the films exhibited (002) predominant orientation with monoclinic structure in consistant with the other reports[4]. The X-ray diffraction spectra of WO_3 films deposited at 873 K and at various oxygen partial pressures on (100) $SrTiO_3$ is shown in figure1. It is observed from the X-ray diffraction spectra that the (002) peak of the WO_3 films overlaps with the (100) substrate peak because of very similar interplanar spacings[5]. The 2θ positions for the (100) peak of $SrTiO_3$ and the (002) peak of WO_3 are observed to be at 22.78 ^{0} and 23.10 ^{0} respectively. A very low intensity of the (020) film peak is also observed in the films, whereas

the (200) peak is not seen in the films. The intensity of the (020) peak decreased with the increase of oxygen partial pressure and was almost diminished at an oxygen partial pressure of 150 mTorr. The diminishing of the (020) peak implies the improved epitaxy. These observations reveal the (00l) plane epitaxy between WO_3 films and (h00) $SrTiO_3$, which suggests that the film planes are crystallographically aligned with the substrate planes. These results are comparable with the epitaxial WO_3 films grown by Garg et al.[3] using dc magnetron sputtering. The surface morphology of the films deposited at 873 K in an oxygen partial pressure of 150 mTorr is shown in figure 2. Iso-epitaxial columnar growth has been observed in the topography of these films. These results indicate that the epitaxial WO_3 thin films grown on $SrTiO_3$ substrates are attractive for NO_x gas sensing applications. These iso-epitaxial WO_3 films for NO_2 gas testing were prepared by evaporating two gold contacts in gap configuration[6]. The contacts were found to be ohmic for a wide range of voltages. The sample under test was placed on to a heated sample holder in a stainless steel cell and exposed to different gas concentrations. A constant flow rate of 100 sccm was maintained with a Tylan mass flow rate controller. The gas to be tested coming from a certified bottles was diluted with dry air to obtain the desired composition. The temperature of the sample was continuously monitored with a thermocouple. The gas sensitivity of WO_3 thin films for 100 ppm NO_2 at various temperatures was measured. The gas sensitivity defined as $\Delta R/R_{air}$ where ΔR is the resistance change of the films upon exposure of NO_2 and R_{air} is the resistance in air. The sensitivity of WO_3 thin films increases with the increasing temperature of the sensor. The maximum sensitivity of WO_3 films deposited at 873 K in an oxygen partial pressure of 150 mTorr for 100 ppm NO_2 was about 150 at an operating temperature of 673 K. The response time to reach 90% of the maximum value of the signal was about 2 minutes.

Pulsed laser deposited WO_3 thin films were found to be highly influence by the substrate temperature and oxygen partial pressure. We have observed that control of the deposition parameters promotes the films stioichiometry, surface morphology and the crystal structure. WO_3 thin films deposited on single crystal $SrTiO_3$ substrates at a temperature of 873 K and in an oxygen partial pressure of 150 mTorr were found to have (001) plane epitaxy between WO_3 thin films and $SrTiO_3$ substrate. The AFM data demonstrated the iso-epitaxial columnar growth in the films.The sensing properties of these films for NO_2 gases were studied to see the applicability of these films for environmental monitoring. The iso-epitaxial WO_3 thin films were found to be more sensitive to NO_2 gas with a sensitivity of about 150 at an operating temperature of 673 K.

1. T.Inoue, K.Ohtsuka, Y.Yoshida, Y.Matsuura and Y.Kajiyama,Sensors and Actuators B 24-25 (1995) 388
2. D.B.Chrisey, G.K.Hubler, Pulsed Laser Deposition of Thin Films (Wiley, Newyork) 1994
3. A.Garg, J.A.Leake, and Z.H.Barber, J.Phys.D.Appl.Phys. 33 (2000) 1048.
4. P.Tagtstrom and U.Jansson, Thin Solid Films 352 (1999) 107.
5. O.M.Hussain, A.S.Swapnasmitha, J.John and R.Pinto, Appl.Phys.A (2004), DOI:10.1007/s00339-004-3041-z
6.O.M.Hussain and K.S.Rao, Materials Chemistry and Physics 80 (2003) 638

PLD GROWN PALLADIUM COATED WO_3 THIN FILMS FOR HYDROGEN SENSORS

M. Krishna Kumar[1] M. S Ramachandra Rao[2] and S. Ramaprabhu[1]
[1]*Alternative Energy Technology, Department of Physics,*
[2]*Material Science Research Center and Department of Physics*
Indian Institute of Technology Madras, Chennai - 600 036, India.
mkkumar@physics.iitm.ac.in , msrrao@iitm.ac.in and ramp@iitm.ac.in

Abstract

Hydrogen is essential in many fields of research and industry, and with the development of fuel cell technology the application prospects of hydrogen are increased. Hydrogen concentrations in air exceeding 4% are easily flammable and are highly explosive, hence detection and monitoring of hydrogen gas has received a great deal of importance. Therefore, a sensor that can detect H_2 gas at ambient conditions is a necessity. This paper presents the fabrication of hydrogen sensors based on the changes in electrical and optical properties of Pd coated WO_3 thin films grown using pulsed laser deposition (PLD) technique. Pd is well known for its catalytic nature towards breaking of molecular hydrogen into atomic hydrogen [1, 2]. WO_3, a well known gasochromic material, when engineered in thin film form with island like growth of Pd will be a good hydrogen sensing material. Pd thin films with different thickness have been deposited on WO_3 coated quartz substrates by PLD and the effect of film thickness on the performance of sensor has been studied. Optimization of the thin film growth condition has been carried out by systematic variation of growth parameters like substrate temperature, laser power density and ambient Ar gas pressure. The morphology and composition of the films have been analyzed by XRD, SEM, AFM and EDAX. In-situ electrical resistance using linear four-probe technique and in-situ optical properties have been measured and their dependence on different concentrations and flow rates of hydrogen gas have been studied and discussed.

References

[1].T. Xu, M. P. Zach, Z. L. Xiao, D. Rosenmann, U. Welp, W. K. Kwok, and G. W. Crabtree *J. Appl. Phys.* 86, 203104 (2005)

[2]. A. Chtanov and M. Gal, *Sens. Actuators, B.* 79 (2001) 196–199.

EPITAXIAL GROWTH OF ZINC OXIDE ON GALLIUM NITRIDE TEMPLATE BY PULSED LASER DEPOSTION

T. Premkumar, P. Manoravi*, M. Joseph* and K. Baskar
Crystal Growth Centre, Anna University, Chennai 600 025, India
** Radiochemistry Laboratory, IGCAR, Kalpakkam 603102, India*
email:prem_cgc@yahoo.co.in

Abstract

Lattice-matched epitaxy and good luminescence properties of ZnO/GaN heterostructures are promising for optical devices. The near perfect lattice alignment of the ZnO epilayers on GaN as compared to those grown directly on sapphire exhibits excellent properties for commercial applications [1]. ZnO epitaxial layer have been grown heteroepitaxially on GaN templates using Pulsed Laser Deposition (PLD) system using Nd:YAG (λ=532nm) laser as a excitation source to ablate ZnO. The power density of the laser was $1x10^8$ W/cm^2. The base pressure of the deposition chamber during the growth was maintained at 8×10^{-6} torr.

The surface morphology of the grown epilayers were studied using Scanning Electron Microscopy (SEM). To study the optical properties the ZnO layers Photoluminescence (PL) and Time Resolved Photoluminescence (TRPL) have been employed. The results of surface morphology of the layers, the full-width at half maximum of photoluminescence spectrum and lifetime of the minority carriers were discussed.

References:

1. R.D. Vispute, M.He, and Y. X. Li "Heteroepitaxy of ZnO on GaN and its implications for fabrication of hybrid optoelectronic devices" Applied Physics Letter, Vol.73, No. 3, (1998), pp.348-350.

Pulsed laser deposited $Y_3Al_5O_{12}$:Ce phosphor thin films for blue light converted white light emitting diodes

M.Kottiasamy[1], P.Thiyagarajan[1,2] M.S.Ramachandra Rao[1,2]

[1]Material Science Research Centre, Indian Institute of Technology – Madras, Chennai-600 036.

[2]Department of Physics, Indian Institute of Technology Madras, Chennai-600 036.

Abstract

$Y_3Al_5O_{12}$:Ce phosphor thin films were deposited on quartz substrate by pulsed laser deposition (PLD) technique. The as-deposited film showed an yellow colour emission with an emission maximum at 550 nm at the blue LED excitation wavelength (465 nm). For the PLD deposition, the required target was prepared from phosphor powder which was obtained by sol-gel method using stoichiometric starting chemicals viz., yttrium nitrate, aluminium nitrate and cerium nitrate and citric acid. This method ensures the homogeneous distribution of Ce and low temperature formation of the YAG. The as formed phosphor was then pressed and sintered at 1200^o C for 24 hours to obtain a dense target for PLD growth. Thin films were grown on quartz substrates at low substrate temperature ~ 700º C in an oxygen partial pressure of 0.32 mbar. The flounce of the laser power was kept at 2.2 Jcm^{-2} during the deposition. X- ray diffraction (XRD) studies confirmed the phase formation. SEM pictures were taken to analyze the surface morphology of the films. Fig.1 shows a luminescent emission of the as deposited YAG:Ce thin film phosphor along with a blue LED emission which results in white light. It is expected that further annealing enhances the crystallinity and PL emission properties of the thin film. Details of thin film growth and PL spectra will be presented and discussed.

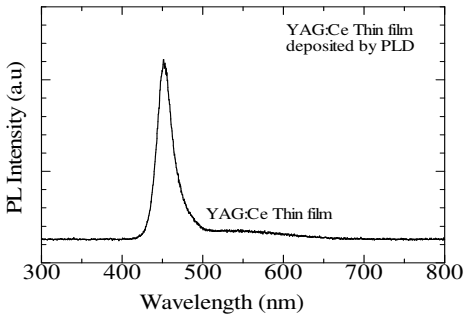


Fig.1.White light emission from YAG:Ce thin film at the excitation of blue LED

Pulsed Laser Deposition of ZnO:Al thin films at room temperature

Manoj R and M.K. Jayaraj*
Optoelectronics Devices Laboratory, Department of Physics, Cochin University of Science & Technology, Kochi-22, India
*Email: mkj@cusat.ac.in

Abstract

The excellent optoelectronic properties of zinc oxide have attracted considerable interest over the past few years. The growth of crystalline ZnO at room temperature would be highly interesting from the point of device development. It has been reported that ZnO can also be made p type by codoping third group elements (Ga, Al etc) and with nitrogen. The development of room temperature thin film growth techniques would be very useful to the optoelectronics industry.

In this paper we report the deposition of highly oriented ZnO:Al thin films by PLD at room temperature. The ZnO films were deposited using Nd:YAG laser with pulse width 6-7 ns and repetition frequency of 10 Hz. The second harmonics (λ = 532nm) as well as the third harmonics (λ = 355nm) were used for depositing the films. Better film morphology and growth rates were obtained when the deposition was carried out using the third harmonics. The substrate to target distance was kept at 6 cm. Oxygen gas was fed into the chamber during the deposition through a mass flow controller (0.003 m bar to 0.008 m bar). The structural, optical and electrical properties of the thin films were studied. The crystal structure of the ZnO:Al thin film was analysed using X-ray diffraction(XRD) technique. The films were deposited at room temperature on glass, fused quartz and plastic substrates. All the films were crystalline and showed good transmittance >85% in the visible range.

Transparent p-$AgCoO_2$/n-ZnO p-n junction fabricated by Pulsed Laser Deposition

R.S.Ajimsha, K.A.Vanaja, M.K.Jayaraj*
Optoelectronics Devices Laboratory, Department of Physics,
Cochin University of Science and Technology, Cochin-22.
*Email: mkj@cusat.ac.in
P Misra and L.M.Kukreja
Thin Film Lab, Centre for Advanced Technology, Indore 452 013.

Abstract

Wide bandgap oxide semiconductors are now being extensively studied for their potential applications for transparent electronics and opto-electronics. Transparent electronic and optoelectronic devices may be realized if sufficiently high conductivity through electrons and holes doping could be achieved in such semiconductors[1]. The wide bandgap oxides of p-block heavy metallic cations with ns^0 electronic configuration (ZnO, In_2O_3 etc) show high conductivity and their mixed oxides can be changed to an n-type by an appropriate doping with donor elements. In practice it is difficult to obtain p-type Transparent Conducting Oxide (TCOs) because of the lower carrier mobility and densities associated with narrow valance bands. The materials that are currently being investigated for the application of p-type TCOs are ABO_2 delafossites where A is the monovalent cation and B is the trivalent anion. p-type delafossite thin films are all so far based on copper delafossites [2]. Several strategies have been adopted to explore the possibilities in the delafossite materials and have been implemented in thin film form. These include varying the trivalent B cation and appropriate dopants and producing new films based on silver rather than copper.

In the present study we report the fabrication of p-n heterojunction using n-ZnO and p-$AgCoO_2$. p-$AgCoO_2$ thin films were deposited by pulsed laser deposition of sintered target of $AgCoO_2$ using third harmonic of a Q-switched Nd: YAG laser with a fluence of 1 J/cm^2 at 355nm, 7ns pulse width and10Hz repetition frequency. The bulk powder of $AgCoO_2$ was synthesized by hydrothermal reaction of $AgNO_3$, Co_3O_4 and KOH in a Parr bomb at 250^0C. The p-n heterojunction diodes were grown with a structure of p-$AgCoO_2$/n-ZnO/n-ITO/glass. Glass substrates coated with a 200nm thick sputtered ITO film had a transparency > 85% in the visible region. The ZnO was deposited over the ITO coated glass by PLD under the conditions mentioned above. The ITO layer forms an ohmic contact with ZnO. The $AgCoO_2$ layer of thickness 200nm had a transmission of about 60% in the visible region. The current-voltage (I-V) characteristics of the junction yielded an ideality factor which was much greater than 2. The I-V characteristics showed that the turn on voltage was 0.75V. The low turn on voltage may be due to the large number of defects and interfacial states. Rectification was observed with a ratio of forward to reverse current of 7 at 1.5V. Further work to improve the quality of the diodes is underway.

References

1. G.Thomas, Nature, 389,907(1997)
2. N.Duan, A.W.Sleight, M.K.Jayaraj, J.Tate, Appl.Phys.Lett, 77,1325 (2000)

Structural, morphological and electrical characterization of InN thin films grown by pulsed laser deposition

S. S. Harchirkar*, A.G.Banpurkar and K. P. Adhi

Advanced Laser Material Processing Laboratory, Centre for advanced studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune India-411 007

P. M. Koinkar, M. A. More, and D.S.Joag

Field ion microscopy and Field emission spectroscopy Laboratory, Centre for advanced studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune India-411 007

L. M. Kukreja

Thin Film Laboratory, Center for Advanced Technology, Indore – 452 013

** Corresponding authors e-mail address: hsanjay@physics.unipune.ernet.in*

Abstract

Indium nitride (InN), so far, is least studied among the III- nitride semiconductors. Recent studies on wurtzite InN have firmly established it to be a narrow band gap (0.6 to 0.7 eV) material[1,2]. This not only enhances the range of emission spectra from deep UV to near Infrared region of III-nitrides, but with emission around 1.55 □m, also becomes a potential candidate for the telecommunication industry [3]. InN has also been demonstrated as a useful material for cost effective solar cells, optical coatings, sensor for chemical and biological applications etc.[4-5]. We have attempted to study thin films of wurtzite InN grown by pulsed laser deposition (PLD) technique on (0001) sapphire from the point of view of cold emission. Excimer-laser (KrF gas; wavelength □ = 248 nm, pulse duration t_p = 20 nsec, repetition rate = 5Hz) was used for the ablation of the commercial Indium (In) target (Kurt J. Lesker – USA, purity 99.99%). The laser fluence on the target surface was kept at about 0.5 J/cm^2. High purity (99.999%) nitrogen was introduced into the chamber and the pressure was maintained at 25mTorr through out the deposition. Discharge in the nitrogen ambient was initiated and maintained by application of 900 V dc across the target holder and a grid placed in between the substrate and target. The substrate temperature was maintained at 500 °C. After the deposition, samples were cooled to room temperature slowly under the same conditions of pressure and discharge.

The thickness of the films, as estimated from Tallystep measurements was ~ 4000Å. The presence of (10$\underline{1}$1) and (0002) planes in X-ray diffraction (XRD) pattern indicates the polycrystalline growth of wurtzite InN. No peaks corresponding to Indium were observed within the detection limit. The surface morphology, RMS roughness and the crystallite sizes were recorded by AFM in the contact mode (Jeol- JSPM 5200). The AFM results show that the InN films are granular in nature and the rms surface roughness is approximately 35 Å

The cold electron emission from the thin films was studied by the technique of Field Emission Microscopy (FEM). In this technique, the film is mounted on an insulating stand and placed in front of a ZnS screen at a distance of ~ 2 mm. The chamber is evacuated to low pressures of the order of 10^{-9} Torr using a sputter ion pump in conjunction with liquid nitrogen trap. High voltage of the order of few kV is applied between the film and the screen in order to study the emission from the films. The field emission current–voltage characteristics were analyzed by using the Fowler–Nordheim (FN) equation;

$$J = 1.54\times10^{-6}\frac{E^2}{\phi\, t^2(y)}\exp\left(-6.83\times10^{7}\frac{\phi^{\frac{3}{2}}}{E}f(y)\right)$$

where *J* is current density, E is applied field, □ is work function of InN respectively. The turn on field [6] defined as the field required to obtain current density of 10 □A/cm^2 is around 3.4V/□m. The FN plot of log(J/E^2) vs 10/V^4 has a linear relation within the measurement range, which confirms that the current results from field emission.

Acknowledgement: The authors, KPA, AVL and LMK thank DAE - BRNS for the financial support to carryout this work.

References

1. J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, W. J. Schaff, Y. Saito, and Y. Nanishi, Appl. Phys. Lett. **80**, 3967 (2002)
2. K. Sugita, H. Takatsuka, A. Hashimoto, and A. Yamamoto, Phys. Status Solidi B **240**, 421 (2003).
3. B. Arnaudov, T. Paskova, P. P. Paskov, B. Magnusson, E. Valcheva, B. Monemar, H. Lu, W. J. Schaff, H. Amoano, and I. Akasaki, Phys. Rev. B **69**, 115216 (2004)
4. Hai Lu, William J. Schaff, and Lester F. Eastman, J. Appl. Phys. **96**, 3577 (2004)
5. Z. G. Qian, W. Z. Shen, H. Ogawa, and Q. X. Guo, J. Appl. Phys. **92**, 3683 (2002)
6. Y. B. Tang, H. T. Cong,a! Z. G. Zhao, and H. M. Cheng, Appl. Phys. Lett. **86**, 153104 (2005)

Study of irradiation induced changes in the morphology and transport properties of $La_{0.7}Sr_{0.3}MnO_3$ thin films

M. S. Sahasrabudhe*, K. P. Adhi, and S. I. Patil

Advanced Laser Material Processing Laboratory, Centre for Advanced Studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune - 411 007, India

Ravi Kumar

Nuclear Science Centre, Aruna Asaf Ali Marg, New Delhi - 110 067, India

** Corresponding authors e-mail address: mandar@physics.unipune.ernet.in*

Abstract

The doped perovskite manganites, with the chemical formula $R_{1-x}A_xMnO_3$, where R and A are rare–earth (La, Nd, Pr, etc.) and alkaline earth (Ca, Sr, Ba etc.) ions respectively, have been the focus of immense study in the recent past[1-3]. With a high Curie temperature T_c of ~ 370 K, $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) appears to be an attractive material for magnetic field sensing and magnetic storage applications at or above room temperature[4]. Controlling / tailoring transport properties of this material is hence of importance. While the oxygen content of the film influences the transport properties drastically, the interfacial strain has little effect as the thickness of the film increases beyond ~ 1000 Å[5]. In the present study, swift ion irradiation of LSMO thin films by 200 MeV Ag ions has been used to create defects and hence, related strain over the entire thickness, which lead to the modifications of structural, electrical and magneto resistance properties.

Highly c-axis oriented magneto resistive films of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) were deposited on $LaAlO_3$ (LAO (100)) substrate by pulsed laser deposition (PLD) technique. During deposition the energy density of the incident radiation on the surface of target was maintained at 2 J/ cm^2 and the substrate temperature was 700 °C. Oxygen was then introduced into the chamber and maintained at a pressure of 400 mTorr during deposition. After deposition, the samples were slowly cooled at the rate of 5 °C/min. to room temperature in oxygen ambient maintained at atmospheric pressure. The films thus deposited were characterized and then subjected to post deposition annealing in air at 800^OC. The structural quality in terms of orientation and phase formation was studied using x-ray diffraction. The films were also characterized by four probe resistivity measurement technique from 400 K down to 125 K. The morphology of the films was studied using Atomic Force Microscopy (AFM). The effect of swift heavy ion (SHI) irradiation on structural and electrical properties of these annealed films has been investigated. 200 MeV silver ions at different dose values ranging from 1×10^{11} to 1×10^{12} ions/cm^2 were used for the irradiation.

Post deposition annealed films show metallic behavior over a wide studied temperature range, which is expected for LSMO films. Irradiated films show the metal-insulator transition. The peak transition temperature 'T_p' of the irradiated films vary systematically, shifting towards room temperature with increasing dose values. The

structural properties also change with the irradiation dose value. The changes in the morphology of these films were studied using AFM. The rms roughness of the film changes with the dose value. These variations were analyzed on the basis of swift ion irradiation induced defects and related strain rather than change in oxygen content of the films.

Acknowledgement: One of the authors MSS would like to thank NSC-Delhi for providing the fellowship under the UFUP program.

* A detailed paper on irradiation study has been communicated to NIMB.

References:

1. K. Chahara, T. Ohno, M. Kasai and Y. Kosono, Appl. Phys. Lett. **63**, 1990 (1993).
2. R. Von Helmolt, J. Weckerg, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).
3. S. Jin, T. H. Tiefel, M. McCromark, R. A. Fastnatch, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
4. T. Venkatesan, M. Rajeswari,Z. W. Dong, S. B. Ogale and R. Ramesh, Philos. Trans. R. Soc. London, Ser. A **356**, 1661 (1998)
5. ″ Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides″ Edt. By C. N. R. Rao and B. Raveau, World Scientific Publication 1998, pg 155 -187

Influence of oxygen variation on the chemical properties of $La_{0.7}Ca_{0.3}MnO_3$ thin films

M. S. Sahasrabudhe, S. K. Date, S. I. Patil and K. P. Adhi

Advanced Laser Material Processing Laboratory, Centre for Advanced Studies in Materials Science and Solid State Physics, Department of Physics, University of Pune, Pune - 411 007, India

Ravi Bathe

International Advanced Research Center for Powder Metallurgy and New Materials, (ARCI) Hyderabad -500 005, India.

S. Kharrazi, R. C. Purandare and S. K. Kulkarni

Surface Physics Laboratory, Centre for Advanced Studies in Materials Science and Solid State Physics,Department of Physics, University of Pune, Pune - 411 007, India

* Corresponding authors e-mail address: mandar@physics.unipune.ernet.in

Abstract

The manganites of the form $La_{1-X}A_XMnO_3$ (A = Ca, Sr, Ba etc., a divalent element) show variety of interesting properties[1-3] amongst which Colossal Magneto Resistance (CMR) is perhaps the most appealing one for the applications such as memory devices, magnetic field sensors etc. The MnO_6 octahedra or Mn – O – Mn network plays an important role in defining the properties in these materials. It has been shown previously that in bulk materials the oxygen stoichiometry plays a crucial role and with increase in oxygen deficiency the peak resistivity temperature decreases where as CMR and the resistivity increases [4, 5]. The present work is focused on the changes in oxygen content of the $La_{0.7}Ca_{0.3}MnO_3$ thin films and its influence on the local chemical environment in these films. X-ray Photoelectron Spectroscopy has been used for this purpose.

Thin films of $La_{0.7}Ca_{0.3}MnO_3$ were deposited on single crystal $LaAlO_3$ (001) substrates by pulsed laser deposition under different oxygen pressure conditions. The LCMO target was prepared by the standard solid-state reaction route, taking high purity (99.99 %) component oxides in their stoichiometric ratios. The single phase LCMO target, as conformed by XRD, was mounted in the chamber such that the polar angle between the incident radiation and the normal to the surface of the target was 45^o. The energy density at the target surface was adjusted to 2 J/cm^2. The substrate temperature was maintained at 650° C throughout the deposition for all the depositions. Films with varying content of oxygen were deposited by changing the oxygen ambient pressure in the chamber viz. 50 mTorr, 100 mTorr, 200 mTorr, 300 mTorr and 400 mTorr. After the deposition, the films were slowly (<5 °C/min) cooled to room temperature at the same oxygen pressure at which they were deposited. The XPS spectra were recorded using the Mk II VG scientific spectrophotometer. Al K□ radiation at 1486.6 eV was used for the study. A hemispherical analyzer having resolution of ~1 eV at pass-energy of 50 eV was used to detect the emitted

photoelectrons. Cleaning of the surface of the films was done by Ar^+ ion sputtering where in the ion energy was 4 keV and the duration of etching was 30 sec.

The XPS data was collected near $La3d_{5/2}$, Ca2p, O1s and $Mn2p_{3/2}$ levels. Studying these spectra illustrates the changes in Mn^{+3}/Mn^{+4} ratio caused due to oxygen variation. $La3d_{5/2}$ peak after deconvolution shows two components; one of lanthanum on the lower binding energy side and a satellite peak on the higher binding energy side. Ca2p peak shows two components one of $2p_{1/2}$ and other of $2p_{3/2}$. As the oxygen pressure during deposition increases the oxygen peak shifts towards higher binding energy side. The de-convoluted peaks of O1s and $Mn2p_{3/2}$ levels further help in understanding the changes in MnO_6 octahedra caused by oxygen content variation. The conversion of Mn^{+4} to Mn^{+3} is a result of reduction in oxygen content of the films has also been established in our case.

Acknowledgement: One of the authors MSS would like to thank NSC-Delhi for providing the fellowship under the UFUP program.

References

1. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993)
2. S. Jin, T. H. Tiefel, M. McCromack, R. A. Fastnacht, R. Ramesh, L. H. Chen, Science **264**, 413 (1994)
3. H. L. Ju, C. Kwon, Q. Li, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **65**, 2108 (1994)
4. G. C. Xiong, Q. Li, H. L. Ju, R. L. Greene, and T. Venkatesan, Appl. Phys. Lett. **66**, 1689 (1995)
5. H. L. Ju, J. Gopalakrishnan, J. L. Peng, Q. Li, G. C. Xiong, T. Venkatesan, and R. L. Greene, Phys. Rev. B 51, 6143 (1995)

Optical and Electrical Characteristics of Lithium Doped Zinc Oxide Thin Films Grown By Pulsed Laser Deposition

N. Bodas[*], B. N. Singh[#], Ravi Kumar,V. K. Dixit, P. Misra and L. M. Kukreja
Thin Film Lab., Center for Advanced Technology, Indore 452 013
[*]*Department of Applied Physics, SGSITS, Indore 452003*
[#]Presenting and corresponding author, Email: bnsingh@cat.ernet.in

Abstract

In recent years, the current interest is to use wide-band gap semiconducting materials for optoelectronic devices applications like blue light emitting diodes, UV laser etc. The Zinc Oxide (ZnO) is a strong and potential candidate for such applications due to its higher band-gap of 3.37eV, high excitonic binding energy of 60 meV at room temperature and having property of a high radiation resistance. Naturally occurring ZnO is predominantly n-type and therefore p-type doping in ZnO is difficult to achieve. For this it is imperative to first suppress the n-type conductivity of ZnO, which is of great importance for various applications. In present report, we discuss structural, optical and electrical characteristics of highly transparent and crystalline lithium doped ZnO (Li:ZnO) thin films on (0001) Sapphire substrates using Pulsed Laser Deposition. The deposition was carried out by using third harmonic (355nm) of Q-Switched Nd-YAG laser, a pulse width of 6ns and 10Hz repetition rate and in an oxygen partial pressure of ~ $1x10^{-4}$ Torr. The substrate temperature was kept at 600ºC and 300 nm thick films were grown at a laser fluence of ~ 2J/cm^2.

The X-ray Diffraction measurement and transmittance spectra of undoped and Li:ZnO thin films with different Li concentration are indicating high crystalline and optical quality of all the films. The behavior of resistivity for ZnO thin films with Li doping concentrations was studied. Resistivity of undoped ZnO film which was ~2 $x10^{-2}$ Ω-cm increased up to ~2 Ω-cm with ~1% of Li doping concentration and then started decreasing with further increase in Li doping. This behavior in resistivity has been attributed to highly mobile Li atoms, as majority of them occupy substitutional positions, thereby acting as acceptors up to concentration of ~1% and beyond this concentration, they occupy interstitial sites, thereby acting as donors. Temperature dependent conductivity (σ) measurements were performed for all the samples in the temperature range of 40-353K to deduce the activation energy of Li doped ZnO using lnσ vs. 1000/T plot. The calculated activation energy was ~15.4 meV for the un-doped film, 49.7 meV for the 1% Li:ZnO film and ~10.5 eV for the 2% Li:ZnO film. For the undoped film, the carrier concentration was estimated ~ $1x10^{19}$/cm^3 at room temperature which dropped to $3x10^{18}$/cm^3 in the case of 0.5% Li doped ZnO thin films. A decrease in the free carrier concentration can be attributed to the fact that Li takes substitutional positions and acts as an acceptor. The variation of carrier concentration with temperature is fairly constant for undoped and 0.5% Li doped ZnO thin films indicating that these films are degenerate throughout the temperature range of measurement. We have observed significant reduction in the conductivity of ZnO thin film with Li doping, which might be put to use in different piezo-electric and opto-electronic devices seeking resistive ZnO. Further studies are underway to explore and understand electrical and photo-luminescence characteristics of Li doped ZnO thin films.

Structural and Optical Characterization Of $Co_xZn_{1-X}O$ Thin Films grown by Pulsed Laser Deposition.

Jabivul J. Sk*, Pankaj Misra, P. K. Sen* and L.M. Kukreja
Thin Film Laboratory, Centre for Advanced Technology, Indore-452 013
**Department of Applied Physics, SGSITS, Indore- 452 003*

*Email: jabivul@hotmail.com

Recently there has been great interest in diluted magnetic semiconductors for their possible technological applications in optoelectronic, magneto opto-electronic and microwave devices. Such applications using III-V semoconductor materials have been demonstrated only at low temperatures because of their low Curie temperature (T_c~110k) [1]. ZnO, a II-VI oxide semiconductor with a direct wideband gap of ~ 3.3 eV at room temperature with the possibility of independent control on spin and charge carriers, is a suitable host material for such applications. In particular, Zinc oxide based thin films doped with transition metal elements like Mn, Co etc. have strengthened the hope of obtaining ferromagnetism at above room temperature [2]. We have studied structural and optical properties of $Co_xZn_{1-x}O$ alloy films grown by Pulsed Laser Deposition. The single wurtzite phase $Co_xZn_{1-x}O$ targets with Co concentrations ranging from 1 to 20 mole % were prepared by mixing CoO (99.997%) and ZnO (99.999%) powders using standard ceramic processing. Thin films were grown at a temperature of 600°C on (0001) sapphire substrates using third harmonic of a Q-switched Nd: YAG laser (355 nm, 10 Hz, and 6 ns) at a fluence of ~ 2 J/cm^2. The films were characterized using X-ray diffraction studies and optical transmission spectroscopy.

The High Resolution XRD of the grown thin films revealed the highly crystalline and c-axis oriented growth without changing wurtzite structure. There were no impurity peaks corresponding to CoO related phase segregation, which indicated the homogeneous distribution of Co in the PLD grown films. The c-axis length and FWHM of (002) ZnO peak increased monotonically with increasing Co composition up to ~ 7%. The optical transmittance spectra measured at room temperature in the spectral range of 200 - 900 nm revealed highly transparent ~ 80% Co-ZnO thin films with a conspicuous mid gap absorption at ~659, 617 and 568 nm respectively due to intra-band Co^{+2} transitions. In order to determine the band gap (E_g) of the films, the absorption coefficient, α^2 was plotted with respect to photon energy and linear portion of α^2 was extrapolated to $\alpha = 0$. The band gap of Co doped ZnO blue shifted monotonically with increasing Co concentration. The similar trend of occurrence of mid-gap absorption due to Co doping was also reported by Tiwari et al. [3]. Further studies in this direction are underway.

References

1. H. Ohno, J. Magn. Magn. Matter. **200**, 110 (1999)
2. K. Ueda, H. Tabata and T. Kawai, Appl. Phys. Lett. , **79**, 988 (2001)
3. S. Ramachandran, A. Tiwari and J. Narayan, App. Phy. Lett. **84**, 5255 (2004)

Growth of Nanostructured Al doped ZnO Thin Films by PLD

K.C. Dubey, Atul Srivastava, Anchal Srivastava+, R.K. Shukla, P. Misra* and L. M. Kukreja*
Department of Physics, Lucknow University, Lucknow-226 007, India
**Thin Film Lab., Centre for Advanced Technology, Indore 452 013*
+ Presenting and corresponding author *Email: vpsri@rediffmail.com*

Abstract

Zinc Oxide, which is a transparent oxide semiconductor with naturally occuring n-type conductivity is emerging as an alternative potential material to Indium tin oxide.This work reports the structural, electrical and optical properties of ZnO and Aluminium doped ZnO (AZO) films deposited on glass substrates at a substrate temperature of 400^0C by PLD using third harmonic Q-switched Nd:YAG laser (355 nm, 10Hz, 6 ns). The oxygen partial pressure was kept at ~ 10^{-3} Torr. The AZO film have Al doping of 2, 3 and 5 atomic percent in ZnO.The θ-2θ XRD patterns of these films show that the prominent peak occurs at 2θ ~ 34^0 and corresponds to (002) diffraction line indicating the presence of hexagonal wurtzite ZnO phase with strong c-axis orientation in all the cases. As the Al doping increased from 0% to 5% a) the nano grain size in the film decreases from ~ 38 nm to ~ 25 nm as determined by full width at half maxima of (002) ZnO peak using Debye-Scherer method, and b) the inter planar spacing of (002) planes of ZnO increases as determined by the XRD peak shift to lower values of θ. Such an effect is probably due to the strain produced by the Al doping. Electrical characteristics of these films were studied at room temperature by I-V and Hall measurements using Vander Paw four point probe method. The resistivity decreased from ~$3x10^{-2}$ Ω-cm for undoped ZnO to ~$6x10^{-4}$ Ω-cm for 2% Al doping. However with further increase in Al doping, the resistivity started increasing. The carrier concentration first increased from a value of ~$7x10^{18}$ cm^{-3} (mobility ~24 cm^2/V-sec) for undoped ZnO to the highest carrier concentration of ~$8x10^{20}$ cm^{-3} (mobility ~13 cm^2/V-sec) at 2% Al doping and then decreased. The electrical conductivity of the AZO film reported here compares favorably well with those reported earlier by others [1,2]. The transmission spectra of these films show an average transmission of ~ 80 % in the visible spectral region. A blue shift in the absorption edge of ZnO with increasing Al concentration in the films is noteworthy as it leads to increase in the width of the transmission window. The bandgap of ZnO and AZO films has been calculated by using α^2 vs $\hbar\nu$ plot. It varies from 3.27eV to 3.67 eV as the Al doping increases from 0% to 5% and the variation is attributed to Burstein-Moss shift. Thus Al doping is doubly beneficial as it increases the average transparency of ZnO film as well as the width of the transmission window.

Acknowledgements AS and RKS thank the UGC New Delhi for financial assistance.

References

1. J. Mass, P. Bhattacharya and R.S. Katiyar; Mat. Sc. & Eng. B103 (2003) 9-15;
2. F. Shan, G.X. Liu, W.J. Lee, G.H. Lee, I.S. Kim, B.C.Shin, Y.C. Kim; J. of Crystal Growth 277 (2005) 284-292

Structural and Optical Characteristics of $Zn_{1-x}Mn_xO$ Thin Films Grown by Pulsed Laser Deposition

U. K. Pandey*, Pankaj Misra & L. M. Kukreja
Thin Film Lab, Centre for Advanced Technology, Indore-452013
**Department of Applied Physics, SGSITS, Indore- 452003*

Abstract

Recently there has been worldwide interest in wide bandgap diluted magnetic semiconductors (DMS) which exploit both the spin and charge of the carriers for the development of transparent spintronic and magneto-optical devices such as spin valve transistors, spin light emitting diodes, and non-volatile storage and logic devices. ZnO with a direct wideband gap of ~ 3.3 eV at room temperature, rugged wurtzite structure and controlled n-type doping is being explored as a host material for such applications [1]. We have deposited $Zn_{1-x}Mn_xO$ thin films with x in the range of 0.01 to 0.3 by Pulsed Laser Deposition technique and studied their optical and structural characteristics. Predetermined amount of ZnO (99.999%) and MnO (99.997%) powders were mixed, calcined at 800^0C for 4 Hrs, pelletised and sintered at 1100 ^{0}C for 2 Hrs for making ceramic targets. Thin films were grown on sapphire (0001) substrates at 600 ^{0}C, in 1×10^{-4} Torr of oxygen pressure using third harmonic of a Q-switched Nd:YAG (Quantel YQ980) laser pulses (335 nm, 10 Hz, 6 ns) at a fluence of about 2 J/cm^2. The distance between the substrate and target was ~ 5.5 cm.

The High Resolution XRD of these films showed only (0002) and (0004) peaks of wurtzite $Zn_{1-x}Mn_xO$ without any peaks corresponding to MnO related phase segregation indicating homogeneous distribution of Mn in the films. The c-axis length of ZnO lattice was found to expand monotonically with the increase of Mn content up to x=0.30. The optical transmittance spectra of these films measured at room temperature in the spectral range of 200 - 800 nm revealed high transparency ~ 80% in the visible spectral region for all the films. The band gap (E_g), of the films was found to increase monotonically with increasing Mn concentration in the film. A significant mid gap absorption, which increased with increasing Mn concentration in the films, was also observed. This dominant mid-gap absorption was assigned as $^6A_1$-$^4T_2$, d-d transitions due to high spin d^5 electron configuration of Mn^{+2} ions in the crystal field of ZnO. The Energy dispersive analysis of the films confirmed that the Mn content in the film was approximately the same as that in the targets. The photoluminescence measurements of $Zn_{1-x}Mn_xO$ thin films with different Mn compositions at 10K revealed a strong luminescence at 368 nm (~3.369 eV) corresponding to $Zn_{1-x}Mn_xO$ band gap which shifted slightly towards blue with increasing Mn concentration in ZnO from 3 - 20% . We also observed an efficient transition at ~ 3.320 eV in $Zn_{1-x}Mn_xO$ thin films which was not present in pure ZnO. This transition has been attributed in literature to the nano clustering of MnO or MnO_2, which are anti-ferromagnetic at 10K [2] or due to an efficient donor-acceptor pair transition as reported by Zang et al in ZnO nanorods [3]. The nano segregations of MnO or MnO_2 are generally difficult to be resolved by High resolution X-ray diffraction but may contribute significantly in luminescence measurements. Further studies are underway to understand the observed results.

References

1. T. Fukumura, Zhengwu Jin, A Ohtono, H Koinuma and M. Kawasaki, Appl. Phys. Lett., **75**, 21,(1999)
2. Mariyana Diaconu et. al., Thin Solid Films, **486**, 117(2005)
3. B.P. Zang et al., Appl.Phys.Lett., **83**,1635, (2003)

Nanostructure Formation of Si and SiO_2 from Laser Ablation of Amorphous Silicon

J Anto Pradeep, Kamlesh Alti, Siddananda Sarma, Pratima Agarwal and Alika Khare*
Department of Physic
Indian Institute of Technology Guwahati, Guwahti 781039
* Corresponding author email: alika@iitg.ernet.in

Abstract

Pulsed laser induced nano structures of Si and SiO_2 formed under vacuum as well as in air are reported in the present paper. High power Q switched Nd: YAG laser was focused on to the amorphous silicon wafer in the vacuum (10^{-5} Torr). The ablated material was deposited on to the microscopic glass slide for the deposition of thin film of nano crystallites of silicon. XRD and AFM studies confirm the formation of particle sizes down to 20nm. The particle size shows the dependence on to the laser power as well as on to the exposure time. The amorphous Si wafers were also exposed to the high power laser directly (unfocused) and show the drastic modification in the surface morphology. The XRD spectrum confirms the formation of nano crystallites of SiO_2 on to the amorphous target. The detail studies of the dependence of the nano crystallite size of Si as well as SIO_2 will be presented in the paper. These studies may find application in designing the waveguide for the optical integrated devices.