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Heteroepitaxial growth and doping of ZnO films for optoelectronic application

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AGENCY REPORT NUMBER****11. SUPPLEMENTARY NOTES****12a. DISTRIBUTION / AVAILABILITY STATEMENT****12b. DISTRIBUTION CODE****13. ABSTRACT (Maximum 200 Words)**

This is the final report of AFOSR grant Number F49620-01-1-0454. No cost extension for one year (31 August/04 to Sept. 1/05) was granted by AFOSR. Summary of the research accomplishments during the total duration 31 August 2001 - Sept. 1/2005 is presented. C-axis oriented ZnO films and nano rods have been grown by rf sputtering and pulse laser deposition (PLD). Thin films of Zn_{1-x}Mg_xO, Zn_{1-x}Al_xO, and magnetic ion substituted ZnMO (M=Co, Mn, Fe, Gd) have been investigated. ZnO, ZnCoO, ZnMnO nano-particles have been synthesized which clearly showed quantum confinement effect. MgO/ZnO multilayer and ZnAlO films deposited by PLD showed c-axis growth and wide band gap above ~6 eV, which is suitable for UV detectors. Mn, Co, and Fe substituted ZnO and ZnS show nearly similar optical behavior, but ZnMnO showed magnetic behavior by SQUID at 5 K. ZnO films could not be doped p-type by rf sputtering, probably due to very high ionization energy required for nitrogen as p-dopant. Several magnetic ion substituted ZnO showed ferromagnetism at lower temperatures, but Zn_xCo_{1-x}Fe₂O₄ (0.4 < x < 0.8) showed room temperature ferromagnetism without change of wurtzite structure of ZnO. The significant results are 1) ZnO/Zn_xCo_{1-x}Fe₂O₄ heterostructure is suitable for the fabrication of spin injection LED and laser. 2) On the basis of studies carried on MgO/ZnO and AlO/ZnO structures, deep UV detectors can be developed. Mn doped ZnO Effective p-doping of ZnO could not be achieved by N doping.

14. SUBJECT TERMS

substituted ZnO, room temperature ferromagnetism, ZnO nanoparticles

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Final technical report of the AFOSR Grant F4962-01-1-0454 (Due 14 September, 2005)

Title: "Heteroepitaxial growth and doping of ZnO for optoelectronic applications, M.S. Tomar (PI), H. Jimenez, Physics Department, University of Puerto Rico, Mayaguez, PR 00681, R.S. Katiyar, Physics Department, University of Puerto Rico, San Juan, PR

Comprehensive technical summary of the significant work accomplished.

This project Grant F4962-01-1-0454 was funded in year 2001 for the duration of three years. On my request AFOSR granted a no cost extension up to 14 June.2005. The progress reports for previous three years had been submitted earlier to AFOSR. In this project is directed to investigate ZnO semiconductor for optoelectronics. The experimental work was focused to growth of ZnO based materials and nanostructures using several growth processes, and p-doping 1) chemical solution based synthesis, 2) rf sputtering, 3) pulse and laser deposition (PLD), 4) plasma enhanced chemical vapor deposition (CVD).

ZnO is a direct gap semiconductor with energy band gap about 3.1 eV. Because of its piezoelectric properties, ZnO is interesting semiconductor for SAW devices. Because of its wide band gap, transparent FETs and UV detector have been developed. Its wide band gap with direct transition makes it attractive for p-n junction based optoelectronic devices such as LED, laser, if effective p-doping is achieved. It may also be useful spin injection LED.

The substitution solid solution in ZnO based materials was investigated in details, and the possibility of p-doping also investigated.

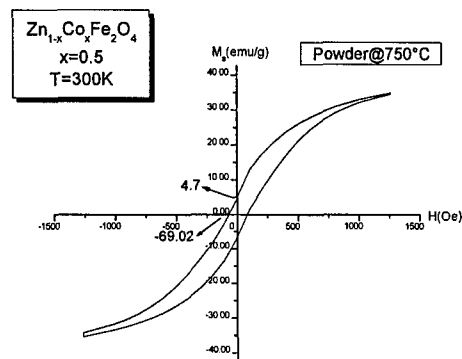
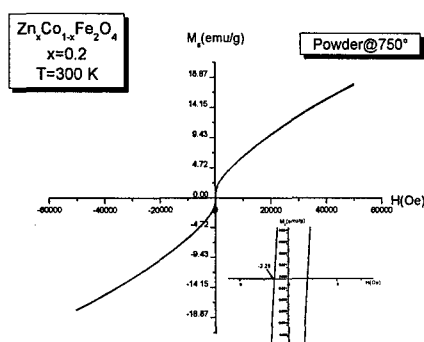
1) $Zn_{1-x}M_xO$ based compounds

The solution chemistry route:

For the synthesis of $Zn_{1-x}M_xO$ compounds, where $M = (Mg, Co, Li, Al)$, the acetate and nitrate salts of the constituent elements and organic solvents 2-ethylhexanoic acid or 2-methoxy ethanol were used. For a particular composition of the compound, i.e. x value in $Zn_{1-x}M_xO$, the 99% pure salts were dissolved in solvent and hot mixed. The transparent solution was refluxed at $110^\circ C$ for about half an hour. Part of the solution was heated to make the powder and other part was used for thin films deposition by spin coating at 3000 rpm. The structural and optical properties of these materials indicate three features, 1) structurally stable materials, and 2) band gap variation. Up to 12% at wt % Mg was incorporated on Zn site without changing the wurtzite structure, but the material showed very low n-conductivity.

Zn substituted ferrites may be effective spin injector in ZnO if they show ferromagnetism. We synthesized several ferrites of the type $Zn_{1-x}Co_xFe_2O_4$, $Zn_{1-x}Mn_xFe_2O_4$, and $Mn(Gd_{1-x}Fe_x)O_4$ and investigated their properties. Recent SQUID measurements show the existence of room temperature ferromagnetism. This indicates that $Zn_{1-x}Co_xFe_2O_4$ can be used as a spin injector in ZnO, so $ZnO/Zn_{1-x}Co_xFe_2O_4$ heterostructures may be used as spin LED emitting in blue region/green region of spectrum. Some M-H curves of $Zn_{1-x}Co_xFe_2O_4$ are shown below.

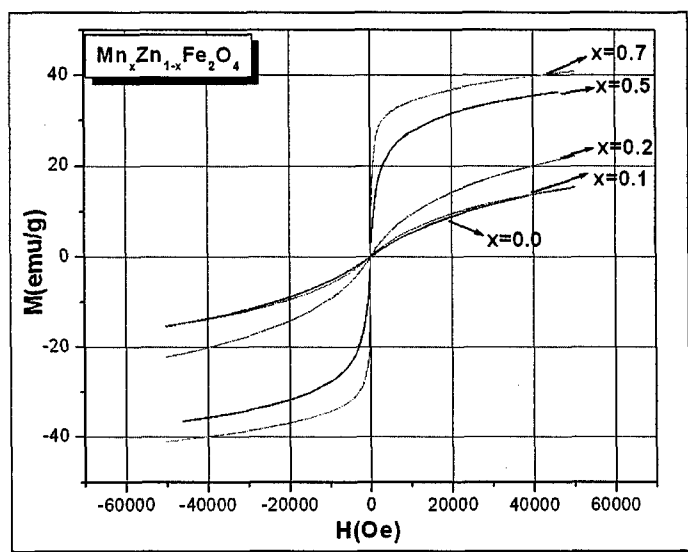
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2) *Thin films by R.F. Sputtering*: Thin films of ZnO and ZnCoO, deposited by rf sputtering, showed c-axis oriented growth on Pt, sapphire, and GaAs substrates as revealed by XRD. The UV spectroscopic ellipsometer, acquired from Sopra, Inc, was mounted on sputtering chamber for in situ growth studies. This ellipsometer measures six Δ and Ψ sets/minute. The ellipsometer output data is fed to the computer to generate real and imaginary values of the dielectric constants as function of photon energy. The real and imaginary parts of the dielectric constants measured on ZnO and ZnCoO films were consistent with the values measured by other methods in literature, indicating the reliability of UV spectroscopic ellipsometer. The work was presented in II-VI semiconductor conference, 2003. The dielectric function vs photon energy curves are shown below. Although sputtered films were c-axis oriented, epitaxial films were not achieved. We planned to use chemical vapor deposition of ZnO with N gas as dopant, but p-type ZnO films could not be achieved. This was probably high energy of formation involved in N bonding. ZnO rod structures deposited during rf sputtering is shown below.

3) *Films by pulsed laser deposition (PLD)*: In order to evaluate the film quality by PLD, effect of strain (post annealing) on the optical and structural properties, was investigated. The result was a) the band gap of ZnO found to unchanged ($E_g = 3.26$ eV) after post annealing, but inhomogeneous distribution of strain was observed as indicated by full width at half minima (FWHM) x-ray rocking curve. Second study was to dope ZnO by magnetic ion during PLD process. $Zn_{1-x}Tm_xO$ ($Tm = Mn, Co, Fe$, and $x = 0.01$) thin films were deposited on Al_2O_3 (0001) substrate in the temperature range of 300 – 600° C with oxygen partial pressure of 10^{-3} to 10^{-5} Torr. The crystalline quality was degraded, but optical absorption showed a band edge shift towards higher energy with increase of Mn content in ZnO. The films were very resistive. Initial result indicates the nanorods by PLD. The PLD deposited $Zn_{1-x}Al_xO$ films showed increased band gap up to 6 eV with n-type conductivity. Possibility of p-doping using nitrogen gas in PLD and rf sputtering did no show any change in conductivity. Both materials were n-type.

4) *Nanoparticles*: Size control synthesis of Mn doped ZnO was performed by a solution process at room temperature. This route is based on dehydration properties of alcohol, using 0.01 M of zinc acetate and manganese acetate dissolved in 50 ml of ethanol at 65 °C. LiOH solution was dissolved in ethanol using sonication and LiOH solution was added to the metal ion solution under vigorous stirring. The particle sizes of 4 to 10nm have been achieved, as revealed by scanning TEM (figure below). X ray diffraction pattern show nanocrystalline nature of ZnO in wurtzite structure. Using Scherrer's equation, crystalline size was estimated to be 6nm. Nanoparticles of several magnetic ion substituted ZnO were also synthesized by co-precipitation route. Broadening of XRD peaks indicates the uniform size nanoparticles. The absorption spectrum shows the blue shifted excitonic peak size dependent optical properties were investigated using UV visible spectroscopy. The optical absorption spectra of ZnO and $Zn_{1-x}M_xO$ ($M = Mn, Co$) shows the effect of particle size increase on the absorption by red shift with time. Photoluminescence (PL) spectra shows two peaks: one is attributed to free exciton emission and another peak is associated to the structure defects such as, interstitials, oxygen vacancy or surface traps. Since Mn^{2+} is a well known luminescent center and shows the characteristic ${}^4T_1-{}^6A_1$ legend field excited state emission (observed in ZnS: Mn^{2+} at 590 nm), but we did not observe it in our samples. Reason seems to be that Mn ion is not incorporated into the core of the ZnO nanoparticle, which is also suggested by SQUID magnetic measurements. Some measured M-H curves on magnetic ion substituted ZnO nanoparticles are shown below.



In the last two years, including the extension period of the research was focused to study magnetic-ion substituted ZnO and related materials for their magnetic behavior, in order to develop the suitable material for ZnO based spin injector devices. The effort was on magnetic ions (Co, Mn, Fe) substituted ZnO and Zn substituted ferrites using different routes.

The significant results are 1) structurally stable $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ and related materials were developed, and 2) room temperature ferromagnetism in $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ has been achieved which shows the possibility of developing spin injection LED and laser devices, 3) multilayer ZnO/MgO and ZnAlO films deposited by PLD have shown a band gap over 6 eV which is ideally suitable for UV detectors. Using N gas, the effective p-doping could not be achieved. Several graduate students indicated below participated in this project for there MS thesis, but Arturo Higalco also worked as graduate training candidate for one year.

Following theses were completed/in progress

M.S. Thesis: "Synthesis, structural, and magnetic characterization of $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$," Rolando Guzman, Physics Department, University of Puerto Rico, Mayaguez, May, 2005 (on record)

M.S. thesis: "Growth and characterization of ZnO with Al doping using pulsed laser deposition" Juan Mass, Physics department, University of Puerto Rico, San Juan, 2002 (on record)

M.S. Thesis: "ZnO based nanomaterials for optoelectronic application," Adrian G. Parra, Physics Department, University of Puerto Rico, Mayaguez (in progress)

M.S. Thesis: "Transition metal doped ZnO films by pulsed laser deposition," N. Awasthi, Physics Department, University of Puerto Rico, San Juan (in progress)

Total Publications/Presentations:

1. "Optical and Ferromagnetic properties of Mn substituted ZnO films for spintronics," R. Guzman, M.S. Tomar, R.E. Melgarejo, O. Perales-Perez (to be presented in MRS Symposium Boston, Dec. (2005).
2. "Structural and magnetic properties of $\text{Zn}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ for potential application in spintronics," M.S. Tomar, R.P. Guzman, R.E. Melgarejo, Indn. J. Phys. (in press)
3. "Nanoscience of oxide materials", Latin American conference on heat and Materials, May 2005, Caracas Venezuela. (Proceedings on CD).
4. "Synthesis and magnetic behavior of nanostructured ferrites for spintronics," M.S. Tomar, S.P. Singh, O. Perales-Perez, R.P. Guzman, E. Calderon, C. Rinaldi-Ramos, Microelectronics Journal **36**, 475 (2005).
5. "Synthesis and characterization of transition ion doped ZnS and ZnO nanostructures," S.P. Singh, O. Perales-Perez, M.S. Tomar, O.V. Mata, APS Conference Proceedings, (Physics of Semiconductors) **772**, 839 (2005).
6. "Room temperature synthesis and characterization of highly monodisperse transition metal doped ZnO nanoparticles," S.P. Singh, O. Prealez, M.S. Tomar, A. Parra, A. Ruiz Mendoza, Proceedings of Nanotech Conference, NSTI-Nanotech 2005, pp 29-32, (2005).

7. "Synthesis and characterization of nanostructured Mn-doped ZnS films and nanoparticles," S.P. Singh, O.J. Perales-Perez, O.V. Matos, *Phys. Stat. Solidi* © 1, 811 (2004).
8. "Study and localized vibration modes in 3d transition metal doped ZnO ceramics and films," N. Awasthi, P. Bhattacharya, B. Sundara.Kannan, R.S. Katiyar, to be presented in MRS fall meeting, Nov.29-Dec.3, (2004).
9. "Synthesis and characterization of ZnO and Mn-ZnO nanocrystals for spintronic applications," M.S. Tomar, O. Perales, S.P. Singh, A. G. Parra, A. Ruiz Mendoza, presented in Amer. Chem. Soc. Symposium, Austin, TX, Nov 3-6, (2004).
10. Effect of transition metal doping in ZnO nano-rods on Si substrate by pulsed laser ablation," P. Bhattacharya, N. Aswasthi, V. Gupta, R.S. Katiyar, presented in XII Intl. Mat. Res Congress, Indianapolis, April 18-21, 2004.
11. "Growth and characterization of ZnO nano-rods on Si substrate by pulsed laser deposition," V. Gupta, P. Bhattacharya, Yu. I. Yuzyuk, and R.S. Katiyar, *Mat. Res. Soc. Symp. Proc.* **818**, M8.26.2 (2004)
12. "Optical properties of transition metal doped ZnO ceramics and thin films," N. Awasthi, P. Bhattacharya, R.S. Katiyar, *Mat. Res. Soc. Symp. Proc.* **825E**, G27.1 (2004)
13. "Comparative study of Mg doped ZnO and multilayer ZnO/MgO thin films," P. Bhattacharya, R.R. Das, R.S. Katiyar, *Thin Solid Films* **447**, 564 (2004).
14. "Ellipsometric studies on ZnO films prepared by rf sputtering," A. Hidalgo, M.S. Tomar, S.P. Singh, in *Physics of Semiconductor Devices*, (K.N. Bhat and A.Das Gupta, Editors), pp. 185, (2003).
15. "Synthesis and characterization of Zn (Mn,Co)O films for optoelectronic applications," A. Hidalgo, E. Melgarejo, and M.S. Tomar, Presented in MRS Symposium, Boston, Sec.1-6, (2002).
16. "Thin films of $Mg_{1-x}Zn_xO$ and $Zn_xCd_{1-x}O$ ternary alloys grown on sapphire using pulsed laser deposition," P. Bhattacharya, D. Quispitupa, J. Mass, R.S. Katiyar, presented in American Physical Society March Meeting, (2002).
17. "Thin films of $Mg_{1-x}Zn_xO$ by multilayer deposition of ZnO/MgO," P. Bhattacharya, Rasmi R. Das, R.S. Katiyar, MRS Meeting, Dec. (2002)
18. "Studies of Mg and Li doped ZnO by solution chemistry and spin coating," A. Hidalgo, R.E. Melgarejo, M.S. Tomar, R.S. Katiyar, presented in MRS Symposium, Boston, Nov. (2001).
19. "On the p-doping structural properties of Zn(Mg, Li)O for optoelectronic devices, A. Hidalgo, M.S. Tomar, F. Aguirre, in *Physics of Semiconductor Devices*," (V. Kumar and B.K. Basu, Editors), pp. 191-193 (2001)
20. "ZnCoO and ZnLiO by solution process," A. Hidalgo, R. Melgarejo, M.S. Tomar, presented in 13th AAAS & Puerto Rico EPSCoR Annual Meeting, Dorado, April 20-22, (2001).
21. "Studies of $Zn_{1-x}Mg_xO$ and its structural characterization," M.S. Tomar, R. Melgarejo, P.S. Dobal, R.S. Katiyar, *J. Mater. Res.* **16**, 903 (2001).