International Journal of Basic and Applied Sciences Vol. 3. No.2. 2014. Pp. 47-51

Full Length Research Paper

Comparative Study of Synthesis of P- type ZnO Nanostructures

Trilok Kumar Pathak#, L.P.Purohit, Amarkant Sharma and R. Kumar
Department of Physics, Gurukula Kangri Vishwavidyalaya, Haridwar

Corresponding author: Trilok Kumar Pathak

Abstract
It is difficult to obtain p-type ZnO because it is naturally n-type semiconductor. In the present work, we have compared different methods of preparation of p-type ZnO viz. molecular beam epitaxy, RF magnetron sputtering and sol-gel techniques. From the literature available, the parameters like carrier concentration, resistivity and Hall mobility, structural and optical properties of p-type ZnO films prepared by different methods were analyzed for the suitability of the material in context of stability and device formation. Among these method, sol-gel method is best to synthesize p-type ZnO due to its low cost, easy precursors, high hole concentration and good approximation with electrical and optical properties.

Key Words: *Molecular Beam Epatixy, Sputtering, Sol-Gel Method, ZnO thin film.*

Introduction

Nowadays several researchers in material science have been focusing attention on searching a viable substitution for materials with wide band gap to be used in a wide range of optoelectronics applications such as GaN [L.P. Dai et. al.]. GaN based short wavelength light emitting devices (LED) and lasers have changed the human life in various ways. ZnO and GaN have been investigated as:

Sr.No.	Material	Structure	Lattice Parameter a	Lattice Parameter c	E_g	Melting Point	Excitation Energy (eV)	Dielectric Constant
1.	[GaN] Gallium Nitrate	Wurtzite	3.189	5.185	3.4	1973	21	5.15
2.	[ZnO] Zinc Oxide	Wurtzite	3.250	5.206	3.37	2248	60	3.72

ZnO has a potential of replacing GaN in semiconducting emitting devices due to its fundamental advantage like the significant large excitation binding energy that produce more efficient excitation emission at room temperature than the case of GaN [Anderson Janotti et. al.].

Zinc oxide is a unique material that exhibits semiconducting, piezoelectric and pyroelectric multiple properties. ZnO is a wide band gap semiconductor of the II-VI compound n-type semiconductor of the periodic table [Muhammad Saleem et. al.]. It has wurtzite structure. In wurtzite structure each unit cell contains four atoms. ZnO has direct band gap of 3.37 eV and a large excitation binding energy of 3.37 eV [Oleg Maksimov et. al.].

The total replacement of GaN is hindered mainly due to the difficulty in achieving reliable p-type conductivity in ZnO with a high hole concentration. However it is difficult to obtain p-type ZnO because ZnO is natural n-type semiconductor and the low solubility of the dopants [Hatice Asil et. al.]. In spite of these difficulties there are report of ZnO doped p-type with N [W Liu et. al.], P [B. Doggett et. al.], As [JC Fan et. al.], Sb [X Pan et. al.] and Li [B Xiao et. al.]. Recently several co-doping techniques have been reported to prepare p-type ZnO film, such as co-doping of nitrogen (N) and gallium (Ga) [Eun Cheol lee et. al.], nitrogen (N) and beryllium (Be) [Y R Sui], N and indium (In) [Jiming Bian et. al.] & N and Aluminum (Al) [T-H Xang et. al.].

There are several method have been applied in the synthesis of p-type ZnO film including chemical vapour depossition (CVD) [FS Sen Chien et. al.], pulsed laser deposition (PLD) [BL Zhu et. al.], molecular beam epitaxy (MBE) [Kwang Gug Yim et. al., Y.W. Heo et. al.], metal organic chemical vapour deposition (MOCVD) [SK Mohanta et. al.], RF magnetron sputtering [W.J. Li et. al., KS Kim et. al.] and sol-gel method [Ziaul Raza Khan et. al., C. Ravichandran et. al., M. Sharma et. al., Y Li et. al.]. In the present work, we have compared different methods of preparation of p-type ZnO viz. molecular beam epitaxy, RF magnetron sputtering and sol-gel techniques.

Description of different properties of p-type ZnO thin films grown by different method

Methodology

Wei-Wei Liu et. al. used molecular beam epitaxy method to synthesized p- type ZnO thin film. Plasma assisted molecular beam epitaxy on Al_2O_3 at 450 ^{0}C, The substrate surface was pre exposure in O-plasma at 500 ^{0}C for 10 min before grown. No gas was used as O source and N dopant and activated during the grown. No gas was used as O source and N dopant and activated during the grown process by an oxford applied research modal HD25 rf atomic source. The NO flux was fixed at 0.8 cubic centimeters per minute at standard temperature. The Zn source temperature was enhanced from 235 to 255 ^{0}C with steps of 5 ^{0}C.

Jain Huang et. al. used Rf reactive magnetron sputtering method to synthesized p- type ZnO thin film. Al-Zn metal is used as a sputtering target in the DC magnetron sputtering system N and O are obtained from nitrogen monoxide (N_2O) and O_2. N_2O is supplied with high enough concentration to get a high concentration of N in the film with O_2 concentration. The effects of N_2O volume ratio and substrate temperature on the conduction type of ZnO films were studied. XRD pattern of ZnO films exhibits a ZnO (002) peak at about 34.5^0. There is no other orientation for the ZnO films were highly oriented.

Yongge cao et. al. used sol-gel method to synthesized p- type ZnO thin film. To prepare P-type ZnO (N doped ZnO) film zinc acetate 2-hydreate [Zn $(CH_3COO)_2$. $2H_2O$] was firstly dissolved into 2-methoxyethanol solution with the sol-stabilizers mono ethanol amine (MEA). Ammonia acetate solution was used as the nitrogen source. The solution was mixed with required percentage reflux at 80^{0}C for 3h. The sols were spin coated on glass substrate at 3000 rpm. The precursor films were pre heated at 280^{0}C for 10 min and then repeated the coating process several times. The crystalline phase and orientation of the ZnO film were determined by x-ray diffraction. It can be observed that the ZnO film exhibit the wurtzite phase with the preferential orientation of (0002).

In above three methodologies the precursors of sol-gel method are easily available and have very low cost. We also need minimum cost equipments and time also. The setup of this method are easily available is the laboratory.

Electrical properties Analysis

Wei-Wei Liu et. al. gives electrical properties of ZnO: N sample grown on (a) a-Al_2O_3 (b) c-Al_2O_3 at various T_{Zn}. These properties described as-

S.N.	Substrate	T_{Zn} (^{0}C)	Resistivity (Ω cm)	Hall mobility ($cm^2V^{-1}s^{-1}$)	Carrier concentration (cm^{-3})	Carrier type
1	a-Al_2O_3	235	0.4	12.68	3.58×10^{18}	n
2	a-Al_2O_3	255	2.6×10^4	0.35	9.53×10^{14}	n
3	c-Al_2O_3	235	3.41	0.52	3.46×10^{18}	n
4	c-Al_2O_3	255	202.14	1.33	2.60×10^{16}	p

Shu-Yi-Tsai et. al. synthesis ZnO films of various N^+ dose densities by Rf sputtering method. The electrical properties of ZnO photodiode were examined by a Keithely 4200/scs digital semiconductor characterization system. The device exhibits a very low dark leakage current upto 4V in the reverse bias configuration. The Hall Effect measurement is shown in following table-

S.N.	Substrate	N^+ ions/ cm^{-2}	Resistivity (Ω cm)	Hall mobility ($cm^2V^{-1}s^{-1}$)	Carrier concentration (cm^{-3})	Carrier type

1	Corning glass	1×10^{17}	1.61×10^{-2}	2.69	2.32×10^{18}	n
2	Corning glass	3×10^{17}	1.05×10^{-1}	1.11	6.84×10^{19}	p
3	Corning glass	5×10^{17}	9.80×10^{-1}	0.87	8.44×10^{19}	p
4	Corning glass	7×10^{17}	7.24×10^{-1}	2.29	2.94×10^{19}	n

Yongge cao et. al. state that two layer structure ZnO homo junctions are also prepared by thin film grown by sol-gel method and a typical rectifying behaviour in I-V curve observed. The Hall Effect measurement of the ZnO, ZnO:N and ZnO:N:In films fabricated given as-

S.N.	Substrate	Sample	Resistivity (Ω cm)	Hall mobility ($cm^2V^{-1}s^{-1}$)	Carrier concentration (cm^{-3})	Carrier type
1	Quartz glass	ZnO	3.571	9.8	-1.78×10^{17}	n
2	Quartz glass	ZnO:N	3.48×10^{-1}	1.3	7.50×10^{17}	p
3	Quartz glass	ZnO:N:In	1.58×10^{-1}	0.6	9.80×10^{17}	p

From above electrically study we can state that in p-type ZnO thin film grown by Rf sputtering method we get maximum carrier concentration and low resistivity. So for electrical application Rf sputtering method have remarkable place to synthesis ZnO thin film.

Optical properties Analysis

Wei-Wei Liu et. al. gives optical properties of ZnO: N sample grown on (a) a-Al_2O_3 (b) c-Al_2O_3 at various T_{Zn}. The optical absorption spectra of ZnO powder and ZnO: N films deposited at 450 ^oC in the visible region start from 370 nm and the absorption of the film in the UV region was stronger. The optical band gap was found to be about 3.262 eV. It benefit for the incorporation efficiency of N in ZnO films.

Jain Huang et. al. investigate that the transmittance spectra od ZnO film grown by RF sputtering method is the function of wavelength in the range 350-850 nm at different N^+ dose densities. PL Spectra reveals that the P-type Zno films had high optical quality. The transmittance decreases with the increasing dose density of N^+ implantation. A sharp absorption edge is observed around 380 nm for all the film indicating a cut off edge of pure ZnO. The average optical transmittance can be as high as 80% is detected in the visible spectrum for the film implemented with various N^+ dose densities. It is noticed that band gap increases with increasing RF power and the value is within the range 3.1~ 3.3 eV.

Yongge cao et. al. observed optical transmittance spectrum of nanocrystalline ZnO: N thin films grown by sol-gel method using UV-Visible from 200 nm- 800 nm. The transmittance is over 80 % in the visible region from 400 nm- 800 nm. Sharp absorption edge is located at 380 nm which is due to the fact that ZnO is a direct band gap semiconductor. We calculate the band gap using the curve between $(\alpha h\nu)^2$ and hν. The band gap is E_g (ZnO) = 3.3 eV, E_g (ZnO:N) = 3.3 eV. The band gap depends on many factors e.g. the nature and concentration of precursors, structural defect and the crystal structure of the films.

For optoelectronics application we need maximum value of transmittance and energy band gap from above discussion we conclude that we get transmittance about 80% and band gap 3.17-3.33 eV in RF sputtering method and sol-gel method. So for this application we can use RF sputtering or sol-gel method to fabricate ZnO thin film.

Summarized Study of different method

From the above discussion of three methods as MBE, Rf Sputtering, Sol- gel we can compare them with respect different parameter. The summarized study of these method can be explain by the given table-

S.N.	Parameter	MBE method	RF Sputtering method	Sol- Gel method	Standard Value
1.	Precursors	Zn- powder N- NO gas	Zn – ZnO target N^+ ions (N_2 gas)	Zn – Zinc acetate N- ammonium acetate	Easley available and low cost preferred
2.	Structure	Wurtzite	Wurtzite	Wurtzite	Wurtzite
3.	Resistivity (Ω cm)	202.14	9.8 $\times 10^{-1}$ (Depends N^+ ion)	3.48×10^{-1}	Minimum value
4.	Carrier concentration (cm^{-3})	2.6×10^{16}	8.44×10^{19}	7.5×10^{17}	Maximum value
5.	Hall mobility ($cm^2V^{-1}s^{-1}$)	1.33	0.87	1.38	Maximum value
6.	Energy band gap (eV)	3.262	3.1- 3.3 (Depends N^+ ion)	3.17	3.1-3.3

Conclusion

From the comparative study we concluded that the precursors of sol-gel method to deposit P- type ZnO thin film are easily available, have low cost and stable at room temperature. The structure of p- ZnO is also wurtzite. The ZnO film prepared by RF sputtering method have lower resistivity and high hole concentration so it have great importance. Sol-gel method as study have remarkable place to synthesis ZnO film for optoelectronics application. In these thin films we get transmittance about 80% and energy band gap 3.17 eV. Thus among these method sol-gel method is best to synthesize p-type ZnO due to its low cost, easy precursors, allowing growth of thin film with large area at low temperature, controllable thickness, desired deposition rate, high hole concentration, optical properties and good approximation with electrical properties.

References

L.P. Dai, H. Deng, F.Y. Mao and J. D. Jang "The recent advantage of research on P-type ZnO thin film" J. Mater. Sci: mater electron, 19; 727-734, 2008.
DOI10.1007/s 110854-007-9398-y.
Anderson Janotti and Charis G Van de walle, "Fundamental of Zinc oxide as a semiconductor" Rep. Prog. Phys., 72, 126501(29pp), 2009.
Muhammad Saleem, Liaang Fang, Aneela Wakeel and C. Y. Kong, "Simple Preparation and characterization of Nano-crystalline Zinc oxide thin film by Sol-Gel method on glass substrate" world Journal of Condensed matter Physics, 2, 10-15, 2012.
Oleg Maksimov "Recent advances and noval approaches of p-type doping of zinc oxide " Rev. Adv. Mater Sci., 24, 26-34, 2010.
Hatice Asil, Kubra Cinar, Emre Gur, Cevdet Coskun and Sebahattin Tuzemen "temperature dependent current voltage characteristics of electrodeposited p-ZnO/ n-Si heterojunction" International Journal of physical Sciences, Vol 8, 371-379, 2013.
W Liu, YD Zhang, YX Wu and SM Zhu "High temperature dehydrogenation for realization of nitrogen doped P-type ZnO" J. Cryst. Growth 310: 3448-3452, 2008.
B. Doggett, S. Chakrabarti and JP Mosnier "Electrical characterization of phosphorus-doped ZnO thin films grown by pulsed laser deposition" Superlattice Microst. 42, 74-78, 2007.
JC Fan, Z Xie, Q Wan and YG Wang "As doped p-type ZnO film prepared by co sputtering ZnO and Zn_3 As_2 targets" J. Cryst. Growth, 307, 66-69, 2007.
X Pan, Z Ye, J Li and Y Che "Fabrication of Sb-doped p-type ZnO thin film by pulse laser deposition" Appl. Surf. Sci. 253, 5067-5069, 2007.
B Xiao, Z Ye, Y Zhang and B. Zhao "Fabrication of p-type Li doped ZnO film by pulsed laser deposition" Appl. Surf. Sci. 253, 895-897, 2006.
Eun Cheol lee, Y.S. kim, Y. G. Jin and K J Chang "First principles study of p-type doping and codoping in ZnO", J. Korean Physical society, 39, 23-26, 2011.
Y R Sui, B Yao, Z Hua G Z Xing and T Wu "Fabrication and properties of B-N codoped ZnO thin films" J. Phys. D: 42, 065101, 2009.

Jiming Bian, Xiaomin Li, Lidong chen and Qin Yao "Properties of undoped n-type ZnO film and N-In codoped p-type ZnO film deposited by ultrasonic spray pyrolysis" Chemical Physics letters 393, 256-259, 2004.
T-H Xang and J. M. Wu. "Thermal stability of Sol-Gel p-type Al-N codoped ZnO homojunction fabricated by spin coating them on ZnO nanoroads" Acta Materialia, 60, 8, 3310-3320, 2012.
FS Sen Chien, CR Wang, YL Chain and RJ Wu. "Fast response ozone sensors with ZnO nanorods grown by chemical vapor deposition" Sensor Actuat Phys. B 144, 120-125, 2010.
BL Zhu, XZ Zhao, FH Su and XG Wu "Low temperature annealing effect on the structure and optical properties of ZnO film Grown by Pulsed Laser Deposition " Vacuum, 84, 1280-1286, 2010.
Kwang Gug Yim, Min Young Cho and Jae Young Leem " ZnO thin film grown on Si (100) substrate with grown interrupted buffer Layers by using plasma assisted Molecular beam epitaxy" J. Korean Physical Sociey, Vol 58, No. 3, PP 520-524, 2011.
Y.W. Heo, K. Ip, S.J. Perton, D.P. Norton and J.D. Budai "Grown of ZnO thin film on c-plane Al_2O_3 by molecular beam epitaxy using ozone as an oxygen source" Applied surface Science, 252, 7442-7448, 2006.
SK Mohanta, DC Kim, HK Cho and S Tripathy "Structural and Optical properties of ZnO nanorods grown by metal organic chemical vapor deposition" J. Cryst. Growth, 310, 3208-3213, 2008.
W.J. Li, C.Y. Kong, H.B. Ruan and L. Fang "Electrical properties and Raman scattering investigation of Ag doped ZnO thin film" Solid state Communications, 152, 147-150, 2012.
KS Kim, HW Kim and NH Kim "Strctural characterization of ZnO film grown on SiO_2 by the RF Magnetron Sputtering" Physica B, 334, 343-346, 2003.
Ziaul Raza Khan, Mohd. Sohab Khan, M. Zulfequar and M. Shahid Khan "Optical and Structural Properties of ZnO Thin Films Fabricated by sol-gel Method" material Science and applications, 2, 340-345, 2011.
C. Ravichandran, G. Shrinivasian, Craig Lennon, S. Sivananthan and J Kumar "Influence of post deposition annealing on the structural, Optical and Electrical properties of Li and Mg doped ZnO thin Film deposited by sol-gel technique" Superlattice and Microstructures, 49, 527-536, 2011.
M. Sharma and R. Mahra "structural, optical, electrical and magnetic properties of sol-gel derived $Zn_{1-x-y}Co_xAl_yO$ films" Material Science Poland, Vol. 26, No. 3, 2008.
Y Li, L Xu, X Li, X Shen and A Wang "Effect of aging time of ZnO sol on the structural and optical properties of znO thin film prepared by sol-gel method" Appl. Surf. Sci. 256, 4543-4547, 2010.
Wei-Wei Liu, Zhen-Zhong Zhang and Cheng-lin –liu "Effect of copressive stress on doping efficiency of nitrogen in ZnO films" Optical Materials 35, 2486-2489, 2013.
Jain Huang, Linjun Wang, Ke Tang and Yiben Xia "Growth of P-type ZnO films and fabrication of ZnO photo diode based UV detectors" Semiconductor Sci. Technology 24, 075025 (5pp), 2009.
Shu Yi Tasi, Yang Ming Lu and Min Hsiung Hon "Fabrication of low resistivity p-type ZnO thin films by implanting N^+ ions" J. Physics, Conference series, 100, 042037 (5pp), 2008.
Yongge Cao, Lei miao and Yasuhiko Hayashi "Low resistivity p-type ZnO films fabricated by sol-gel spin coating" Applied Physics Letters, 88, 251116 (4pp), 2006.