Raman Analysis of Ni Doped ZnO (Ni:ZnO) Thin Films By Sol-Gel Spin Coating System For Device Applications

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Abstract: **Ni doped ZnO thin films were successfully deposited on ITO coated glass substrates by sol-gel spin coating method. The effect of film thickness on the structural properties of Ni:ZnO thin films were investigated by means of X-ray diffraction (XRD) and Raman spectroscopy. The XRD study reveals that the deposited Ni:ZnO thin films were crystallized in hexagonal wurtzite crystal structure with preferred orientation along the (002) plane. Two dominant characteristics modes identified at 484 cm-1 and 570 cm-1. The mode assigned at 484 cm-1 is associated with ZnO non-polar high-frequency E2H mode which confirms the hexagonal wurtzite phase of deposited thin films. The Raman mode at 570 cm-1 correspond to the A1(LO) mode and it exhibited a significant red-shift shift from 580 cm-1 to 570 cm-1 which indicates that a large number of defects (i.e., zinc interstitials and oxygen vacancy defect states) were present in the deposited Ni doped ZnO thin films. The characteristics peaks centered at 1090cm-1 and 936 cm-1 are associated with substrate and organic solvent, respectively. The relative change in the intensity of the Raman modes with corresponding film thickness is attributed to the resonance Raman Effect. The prepared Ni doped ZnO thin film will be used for diluted magnetic semiconductors (DMS) applications.**

Keywords: **Ni:ZnO Thin Films, Optical Material, Thin films, Optoelectronic Devices, Semiconductor Oxide, DMD, Sol-gel.**

I. INTRODUCTION

ZnO is an important II-VI group semiconductor material which is having direct band gap (3.4 eV), large free-exciton binding energy (60 meV) and having high mechanical and thermal stabilities. Its hexagonal wurtzite crystalline (c = 5.21 Å and a = 3.25 Å) form makes it similar to GaN material which is efficiently and widely used in high-performance optoelectronic devices like LED, Laser, optical waveguide, optical amplifier, optical switch, photonic crystals etc. In addition, the abundance of Zn makes it one of the most promising materials among the other transparent conductive semiconducting oxides (TCOs) for large scale applications like front optical window electrode for solar cell and various display based devices. The high photoconductivity, considerable piezoelectric and pyroelectric properties makes it suitable for making high sensitive photodetector and piezoelectric generator and receptor [1-10].

In recent years, the manipulation of the electronic spin in semiconductor devices (spintronics) gives rise to new possibilities for a variety of applications, such as non-volatile memory, quantum computing & communication, solid state devices, magneto-optical communication devices, spin-FET and spin-LED, etc. The future of efficient spintronic devices is based on the preparation and characterization of a material that combines the desirable properties of ferromagnets and semiconductors. Diluted magnetic semiconductors (DMS) also referred to as semimagnetic semiconductors, are alloys whose lattices are made up in part of substitutional magnetic atoms. In contrast to magnetic semiconductors, DMS offer the possibility of studying magnetic phenomena in crystals with a simple band structure and excellent magneto-optical and transport properties. The idea of a DMS, where a small (<10%) concentration of magnetically active atoms (most often Mn although Co and Cr have also been used occasionally) is distributed at the cation sites of the host

semiconductor, is appealing because such a system may have both semiconducting and ferromagnetic properties. However, making such materials has been problematic because the magnetic transition metal (i.e.Mn) is not thermodynamically stable in the semiconductor host (i.e. GaN) and tends to segregate. Existing techniques for semiconductor heterostructure formation enable incorporation of DMS layers into transistors, quantum wells and other electro-optical devices in which the spin splitting can also be tuned by the confinement energy and the size quantization [11-20].

The main thrust of the researchers in this field is to achieving room temperature ferromagnetism in the DMS. The most challenging task for broad applications is to find magnetic or diluted magnetic semiconductors which would operate at room temperature. GaN and ZnO appear to be the most promising materials to have Curie temperature at and above room temperature, but the low solubility of transition metal impurities in GaN, incorporation of transition metal ions is a considerable challenge. ZnO is on the most promising DMS material and it has received increasing attention due to its broad applications and its many desirable material properties. For realizing practical devices, a key requirement is that the host material be ferromagnetic at or above room temperature. Large variations in magnetic properties for Ni–ZnO indicate that ferromagnetism of such a system strongly depends on the methods and conditions used in the preparation. Therefore, studying the influence of doping concentration on ferromagnetism is particularly necessary and effective for clarifying the intrinsic origin of ferromagnetism. Due to outstanding optical properties, considerable attention has been focused on ZnO-based DMSs in the past years. Recently, it has become very essential to investigate the magnetic characteristics and possible mechanisms in ZnO doped thin films with different transition metals such as Mn, Ni, Cu, Cr, and Co [21-26].

ZnO doped with transition metal ions (Ni, Mn, Fe and Co) have attracted much attention for their versatile applications. ZnO Thin films, doped with transitional metals such as Cr, Fe, Co and Ni may exhibit ferromagnetic ordering with T_c above room temperature. Among the transition metal ions, Ni is the most efficient doping elements to improve and tune the optical, electrical and magnetic properties of ZnO thin films. Only few studies of ferromagnetism have been reported on Ni–ZnO system since its preparation is particularly challenging due to the large driving force for phase segregation into NiO and ZnO. Large variations in magnetic properties for Ni–ZnO indicate that ferromagnetism of such a system strongly depends on the methods and conditions used in the preparation. In some cases, even the conclusion of intrinsic ferromagnetism remains controversial. Therefore, studying the influence of doping concentration on ferromagnetism is particularly necessary and effective for clarifying the intrinsic origin of ferromagnetism [27-30].

There are various methods for preparing Ni doped ZnO thin films such as sol gel, spin coating, dip coating, spray pyrolysis, chemical bath deposition, pulsed laser deposition, sputtering. The sol-gel process is one of the most attractive techniques for the thin film deposition because of non-vacuum requirement, low temperature processing, easy to dope and also offers the possibility of preparing large area coating. Also, the thin films by sol gel technique have good homogeneity, excellent compositional control with good electrical and optical properties. Sol gel process has the unique advantages of allowing the preparation of materials of the same composition in different physical forms, coating by varying experimental conditions. Nickel doped zinc oxide (Ni:ZnO) films have been actively investigated by many research groups because they have potential applications in opto-electronic devices such as solar cells, flat panel displays and transparent heat mirrors. ZnO films doped with transitional metals, for example, Co, Ni, Fe, have been widely studied as diluted magnetic semiconductors [31-33]. In this work, we have reported the synthesis and Raman analysis of Ni-ZnO thin films.

II.   EXPERIMENTAL

Pure and Ni doped zinc oxide thin films were prepared by sol-gel spin coating method on ITO coated glass substrates. All the chemicals used were of AR grade (Sigma Aldrich) and were used as received without further purification. The sol solution was prepared by dissolving 0.82406g ($Zn(CH_3COO)_2$, $2H_2O$) Zinc Acetate in to 5ml of 2-methoxymethanol at room temperature and then 0.0093 g Nickel acetate Hexahydrate were added in to it. The Monoethanolamine (MEA) was used as stabilizer of the sol solution. In order to complete the reaction process between the materials in the solution, the prepared solution was vigorously stirred for 2h at 60 °C temperature. After stirring the solution were aged for 24 h at room temperature. The ITO coated glass substrates were used as substrates. The film depositions were done at room temperature by spin coating. Prior to the deposition, the glass substrates were cleaned using acetone, methanol, deionized water and finally, it was sonicated in an ultrasonicator. After cleaning substrate the sol solution was spin coated on the glass substrate at 3000 rpm for 35 sec using the spin coater system (Apex Instrument). The processes were repeated to obtain thin films of 10, 20, 30 layers on the substrate. After the deposition of each layer, the deposited layer was dried at

80 °C for time 10 to 15 sec. After successfully deposition, all the deposited Ni:ZnO thin films were placed in a high temperature furnace and annealed at 500 °C temperature for 1.0 hour to transform amorphous nature to crystalline nature of the thin films. The structural phase identification of the deposited Ni :ZnO thin films were observed through the X-Ray diffraction with CuKα radiation. The Raman spectra were taken using a Micro Raman Spectrometer (Cornes Tech. STR-500) using a He-Ne laser of 633nm (15mW) wavelength. The resolution of Micro Raman Spectrometer is 0.39 cm^{-1}/W at 532nm and 0.71cm^{-1}/W at 633nm, respectively. All the measurements were performed in air.

III.   RESULTS AND DISCUSSION

Raman spectroscopy is a fast, versatile and nondestructive characterization technique which is extensively applied for the characterization of low-dimensional systems such as thin films, nanowires and nanocrystals. It is used for detecting the incorporation of dopants, defects and lattice disorder in the host lattice. The various properties of prepared samples such as amorphous to crystalline phase transitions, oxygen defects, stress states and quantum size effects in transition-metal oxides of a specimen can be analyzed appropriately using this technique [34-39].

ZnO is a II–VI semiconductor that crystallizes in the hexagonal wurtzite structure, which belongs to the C_4 6v (P63mc) space group. The group theory of the pure Zno thin films predicts the existence of the zone centered optical phonon modes A1 +2B1 +E1 +E2. The A1, E1 and E2 modes are called Raman active modes. In addition, A1 and E1 are infrared active, and therefore they split into longitudinal and transverse optical component (LO and TO). The pure ZnO sample phonon modes belong to the 2E2, 2E1, 2A1 and 2B1 symmetries. The two B1 symmetry modes are not Raman active. Generally, in the Raman spectrum of zinc acetate dihydrate bulk the mode at 434 cm^{-1} assigned the Zn-O bond. The mode appears at 936cm^{-1} to the A1 mode corresponding to the bond C-C vibration present in the organic radical (CH$_3$COO−) of the zinc acetate dehydrate. On dissolving the zinc acetate in the ethanol, the E2 mode at 434 cm^{-1} is exalted compared to the bulk zinc acetate [40-44].

Fig. 1 shows the room-temperature Raman spectrum of the Ni-doped ZnO thin films for different thickness (10, 20 and 30 layers). It is obvious from the figure that there are three dominant characteristics peaks appear at 484 cm^{-1}, 570 cm^{-1} and 1090 cm^{-1}. However a slight intense peak centered at 936cm^{-1} is also seen. The peak assigned at 484 cm^{-1} is corresponded to the ZnO non-polar high-frequency E2H mode. This mode represents the band characteristic of the hexagonal wurtzite phase. Basically the E2 mode shifts from 434cm^{-1} to 484cm^{-1} in the zinc acetate solution, this may be due to the presence of Ni in the ZnO crystalline lattice and relaxation of the intermolecular stress [45-49].
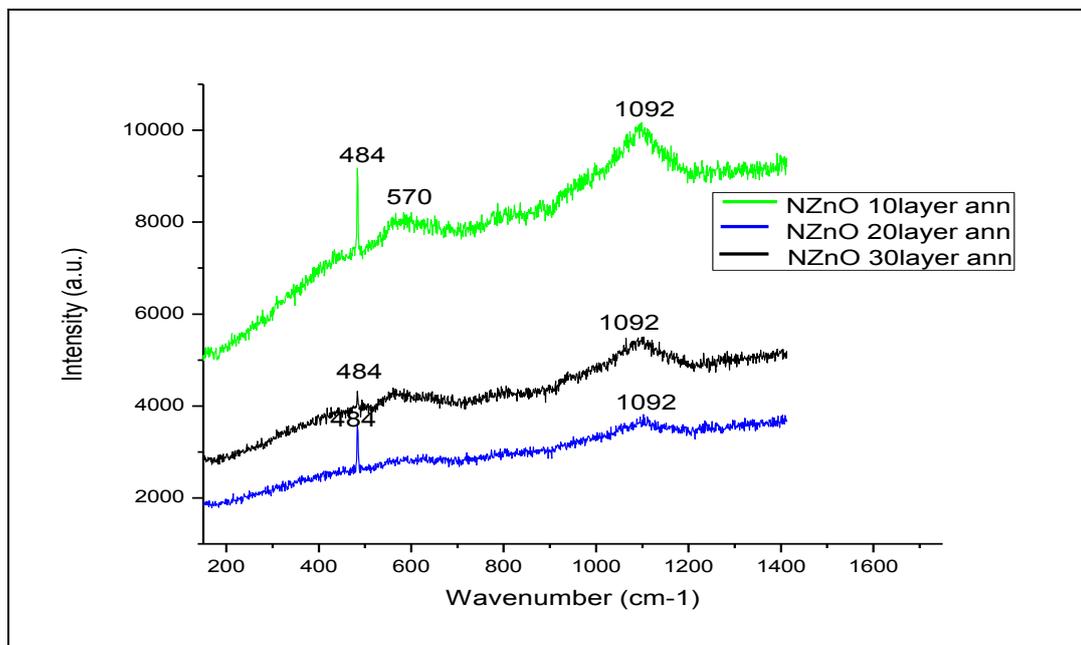
Fig 1: Raman spectra of Ni:ZnO thin Films deposited for different thickness (10, 20 and 30 layers annealed at 500 ^{0}C)

The Raman peak at 570 cm^{-1} belonged to the A1(LO) mode and it may also indicates the presence of Ni in the crystalline lattice. These bonds probably would initiate crystallization process during the films heat treatment. The peak centered at 570 cm^{-1} exhibited a significant red-shift from the wurtzite characteristic vibrational mode centered at 580 cm^{-1}. This shift

clearly showed that a large number of defects (i.e., zinc interstitials and oxygen vacancy defect states) were present in the deposited Ni doped ZnO thin films. The peaks centered at $1072cm^{-1}$ and $936cm^{-1}$ are correspond to the glass substrate and C-C vibration mode present in the organic radical (CH_3COO-) of Ni:ZnO thin films, respectively. It is obvious from the figure that the characteristics modes centered at $484cm^{-1}$, $570cm^{-1}$, $1090cm^{-1}$ and $936cm^{-1}$ are sharp and intense and as thickness increases they becomes broad and dull. This indicates that as thickness of deposited films increases the defect density increases in the deposited Ni:ZnO thin films. Also, it is obvious from the figure that no other additional vibrational mode corresponding to a secondary phase is present which confirms that Ni have been successfully doped into the hexagonal wurtzite structure of the Ni: ZnO thin films. These results were consistent with the XRD results [50,51].

IV. CONCLUSION

Nickel doped zinc oxide (Ni:ZnO) thin films were deposited by sol–gel spin coating system. The deposited thin films were characterized for its structural characteristics using XRD and Raman spectroscopy. The X-ray diffraction indicates that the Ni:ZnO films are crystalline in nature and have preferential orientation along (002) planes with the hexagonal wurtzite structure. The evolution of the Raman spectra of the Ni doped ZnO thin films indicate the hexagonal wurtzite structure formation of ZnO thin films. The characteristics modes centered at $484cm^{-1}$, $570cm^{-1}$, $1090cm^{-1}$ and $936cm^{-1}$ are sharp and intense at low thickness and as increases they becomes broad and dull. This indicates that as thickness of deposited films increases the defect density increases in the deposited Ni:ZnO thin films. The relative change in the intensity of the Raman modes with corresponding film thickness is attributed to the resonance Raman effect. No other additional vibrational mode were present in the deposited Ni:ZnO thin films which corresponds to the absence of the secondary phase in the deposited films and hence, the Ni had been successfully doped into the hexagonal wurtzite structure of the ZnO host crystalline lattice.

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REFERENCES

[1]   Baijun Zhang and Y. Liu ; Chin. Sci. Bull.; 59 (12) (2014) 1251-1275

[2]   Wong, KM, Zou, XB, Chen, P; IEEE Electron Device Lett, 31(2010)132-134

[3]   Chen, T, Wang, Y, Xiang, P; Appl Phys Lett 100 (2012) 241112

[4]   Lau, KM, Wong, KM, Zou, XB; Opt Express 19(2011) A958-A961

[5]   Dolmanan, SB, Teo, SL, Lin, VK; Electrochem Solid State Lett 14(2011) H460-H463

[6]   R.K. Pandey, Swati Mishra, Avik Karmakar, M.P. Sharma and P.K. Bajpai, Journal of Pure Applied and Industrial Physics, Vol.5(10) (2015)289-297

[7]   R.K. Pandey, Swati Mishra, Avik Karmakar, M.P. Sharma and P.K. Bajpai; Journal of Pure Applied and Industrial Physics, Vol.5(10), 305-311(2015)

[8]   Ohno, H. *et al. Appl. Phys. Lett.* 69, 363–365 (1996).

[9]   Wang, M. *et al. Appl. Phys. Lett.* 93, 132103 (2008).

[10] Dietl, T. *Nature Mater.* 9, 965-974 (2010).

[11] Ohya, S., Takata, K. & Tanaka, M. Preprint available at http://arxiv.org/abs/1009.2235 (2010).

[12] Richardella, A. *et al. Science* 327, 665–669 (2010).

[13] Interview with S. Chambers. *Nature Mater.* 9, 956-957 (2010).

[14] Zener, C. *Phys. Rev.* 81, 440–444 (1951).

[15] Ohno, H. *et al. Nature* 408, 944–946 (2000).

[16] Zunger, A., Lany, S. & Raebiger, H. *Physics* 3, 53 (2010).

[17] Interview with N. Samarth. *Nature Mater.* 9, 955-956 (2010).

[18] Ohno, H. *Nature Mater.* 9, 952–954 (2010).

[19] Parkin, S. S. P., Hayashi, M. & Thomas, L. *Science* 320, 190–194 (2008).

[20] H.J. Lee, S.Y. Jeong, C.R. Cho, C.H. Park, Appl. Phys. Lett. 81 (2002) 4020–4022.

[21] W. Prellier, A. Fouchet, B. Mercey, ch. Simon, B. Baveau, Appl.Phys. Lett. 82 (2003) 3490–3492.

[22] T. Wakano, N. Fujimura, Y. Morinaga, N. Abe, A. Ashida, T. Ito, Physica E 10 (2001)260–264.

[23] Y.E. XiaoJuan, H.A. Song, W. Zhong, Q.I. Xiaosi, Appl. Phys. 53 (2010) 293–296.

[24] M. Snure, D. Kumar, A. Tiwari, Appl. Phys. Lett. 94 (2009) 012510–012512.

[25] Wakano, N. Fujimura, Y. Morinaga, N. Abe, A. Ashida, T. Ito, Physica E 10 (2001) 260–264.

[26] H.J. Lee, S.Y.Jeong, C.R. Cho, C.H. Park, Appl. Phys. Lett. 81 (2002) 4020–4022.

[27] W. Prellier, A. Fouchet, B. Mercey, ch. Simon, B. Baveau, LAppl. Phys. Lett. 82 (2003) 3490–3492.

[28] S. Ghosh, et el Appl. Phys. A: Materials Science & Processing 90 (2008) 765.

[29] A. Yildiz, et al. Sci: Mater Electron 22 (2011) 1473.

[30] O. Lupan, S. Shishiyanu, L. Chow and T. Shishiyanu, Thin Solid Films 516 (2008) 3338.

[31] Y. E. X. Juan, et al. Scinence China: Technological Sciences 53 (2010) 293.

[32] Y. Xiaolu, et al Yude Physica B:Condensed Matter 406 (2011) 3956.

[33] B. Pandey, S. Ghosh, P. Srivastava, D. Kabiraj, T. Shripati and N. P. Lalla, Phys. (2009) 1164.

[34] Y. Djaoued, S. Badilescu, P. V. Ashrit, D. Bersani, P. P. Lottici,

[35] R. Bruning, *J. Sol-Gel Sci. Technol.* 2002, *24*, 247.

[36] J. C. Parker, R. W. Siegel, *J.Mater. Res.* 1990, *5*, 1246.

[37] G. J. Exarhous, N. J. Hess, *Thin Solid Films* 1992, *220*, 254.

[38] D. Bersani, P. P. Lottici, X.-Z. Ding, *Appl. Phys. Lett.* 1998, *72*, 73.

[39] M. Ivanda, et al J.Mol. Struct. 1999, 480–481, 641.

[40] RajCJustin,JoshiRK,VarmaKBR.CrystResTechnol2011;46:1181.

[41] Duan LB,ZhaoXR,LiuJM,WangT,RaoGH.ApplPhysA2010;99:697.

[42] Aljawfi RN, RahmanF,BatooKM.JMagnMagnMater2013;332:130.

[43] Serrano J, RomeroA H,ManjonFJ,etal..Phys Rev B 69 (2004)094306–14.

[44] Y. Huang, M. Liu, Z. Li, Y. Zeng, S. Liu, Mater. Sci. Eng. B 97 (2003) 111–116.

[45] Y.F. Lu, H.Q. Ni, Z.M. Ren,W.J.Wang, T.C. Chong, T.S. Low, J. Laser Appl. 12 (2000) 54–58.

[46] F. Decremps, J. Pellicer-Porres, A. Marco Saitta, J.C. Chervin, A. Polian, Phys. Rev. B 65 (2002) 092101–092105.

[47] F.J. Manjoˊ n, B. Marıˊ , J. Appl. Phys. 97 (2005) 053516.

[48] J.M. Calleja, M. Cardona, Phys. Rev. B 16 (1977) 3753–3761.

[49] S.H. Jeong, J.K. Kim, B.T. Lee, J. Phys. D: Appl. Phys. 36 (2003) 2017–2020.

[50] C.A. Arguello, D.L. Rousseau, S.P. Porto, Phys. Rev. B 181 (1969) 1351–1363.

[51] L. Wang, Y. Pu, Y.F. Chen, C.L. Mo, W.Q. Fang, C.B. Xiong, J.N. Dai, F.Y. Jiang, J. Cryst. Growth 284 (2005) 459–463.