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SPATIAL CONFINEMENT OF OPTICAL PHONONS IN ZNO NANOWALLS AND NANORODS

M. Arora, R.P. Pant

National Physical Laboratory,
Dr. K.S. Krishnan Road, 110 012, New Delhi, India
E-mail: marora@nplindia.org

FT Raman spectrum of ZnO *nanowalls and nanorods showed optical phonon and multiphonon peaks of* E_2 (*high*) *and* E_2 (*low*), E_1 (*TO and LO*) *and* A_1 (*TO and LO*), $2E_2$, [E_2 + A_1(*LO*)], [E_1 (*LO*) + A_1(*TO*)] *and* [E_1(*TO*) + A(*LO*)] *modes at* (108.9 *and* 434.46 cm^{-1}), (415.24 *and* 583.32), (383.49 *and* 574.84), 215.43, 676.24, 956.02 *and* 998.98 cm^{-1} *respectively. In nanowalls, the appearance of* B_2 *Raman inactive mode at* 276.46 cm^{-1} *is attributed to the existence of built in electric field in the crystallites of* ZnO. *The weak bands at* 516.78 *and* 467.56 cm^{-1} *confirmed the presence of highly localized modes near the grain boundaries having electric field within the grains close to grain boundary The broadening and asymmetry of the first order* E_2 (*high*) *optical phonon mode reveal the spatial confinement of optical phonons.*

Keywords: *NANOWIRES, ZINC OXIDE, RAMAN SPECTROSCOPY, II-VI SEMICONDUCTOR.*

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1. INTRODUCTION

ZnO is a wide band gap semiconductor and exhibits a variety of one dimensional (1D) nanostructures. Among these nanostructures, ZnO nanowalls and nanorods have received much attention with the possibility to form the basis of next generation electronics, photonics and other applications. Currently, there is a great interest in the methods of creating nanostructures on surfaces by various self-organizing techniques. The quantum confinement effect helps in understanding the important electronic and optical properties of ZnO nanowires.

The stability of ZnO film has made it suitable to consider as an alternative to tin oxide and indium tin oxide films, whose electrical and optical properties degrades in hydrogen plasma. Nanostructured ZnO thin films can be grown by different methods such as pulsed laser deposition, spray pyrolysis, sputtering, electrochemical deposition, sol-gel, chemical vapor deposition etc. In these investigations, we have deposited ZnO films on, p type – Si (100) wafer using 5 % and 25 % zinc acetate sol concentration by sol-gel process. This is a very simple and economic process through which the film composition can be easily controlled and deposited over large area with consistent properties. The aim of these studies was to grow nanostructured ZnO films with different sol concentration and characterize their structural, morphological and phonon properties by different spectroscopic techniques.

2. EXPERIMENTAL MEASUREMENTS

2.1 Synthesis of ZnO nanowalls and nanorods on silicon substrate by sol-gel method

Thin films of ZnO were deposited on p-type silicon substrate by sol-gel method. 5 % and 25 % concentration of analytical grade zinc acetate dihydrate, 2-methoxyethanol and monoethanolamine (MEA) reagents were used as reaction starting material, solvent and stabilizer respectively to form the precursor solution. This sol solution was dropped on the p-type silicon wafer with the help of syringe and then rotated in the spin coating unit with 3000 rpm for 30 sec. After the film deposition, these as deposited films were immediately dried at 80 °C for 10 minutes to dry and remove unreacted organic compounds through evaporation. This whole process was repeated ten times to obtain desired thickness of ZnO film. Then this deposited film was post annealed at 300 °C for one hour to thermally decompose ZnO sol and crystallization of deposited film in preferred orientation. The thickness of these deposited films was of the order of – 300 nm.

2.2 Characterization of ZnO thin films nanowalls and nanorods

XRD patterns of these ZnO films were recorded on D8 Advanced Bruker Axs X-ray powder diffractometer by using CuKα radiation at 30 kV, 30 mA in 15-75 ° 2θ range. The surface morphology of these nanostructured zinc oxide thin films were characterized by LEO 440 SEM spectrometer. Perkin Elmer GX 2000 FT-Raman spectrophotometer was used to investigate the various Raman phonon modes obtained in these films spectra at ambient temperature in 3500-100 cm $^{-1}$ region.

3. RESULTS & DISCUSSION

XRD spectra of the 25% zinc acetate sol derived ZnO film deposited on p - type Si wafer as shown in Fig. 1 exhibits the three strong peaks of (100), (101) and (002) orientation planes along with other different weak intensity peaks of ZnO wurtzite. This reveals that the grains of zinc oxide grow along different directions. All these peaks are attributed to the diffraction lines pertaining to the wurtzite structure. The mean crystallite size in these films was determined by using Scherrer's formula. The crystallite size of these films varies in the range of 10-25 nm.

These micrographs exhibited the uniform distribution of microstructures without any cracks and voids with the variation in particle size and their packing density on different substrates.

FT Raman spectrum of 5 % sol derived ZnO nanowalls recorded in 3500-100 cm $^{-1}$ region is shown in Fig. 3. The spectral analysis revealed that optical phonon peaks of E_2, E_1 (TO and LO) and A_1 (TO and LO) modes are observed at (108.9 and 434.46 cm^{-1}), (415.24 and 583.32) and (383.49 and 574.84) respectively. The shift, broadening and asymmetry of E_2 (high) mode depends upon phonon localization by intrinsic defects, laser power used for nanostructure ensembles and spatial confinement within nanostructure boundaries [1-3]. The frequency shift of phonon caused by the defects is not size dependent. As there is a minor shift in the E_2 (high) peak position at same laser power 100 mW in both the nanostructures which

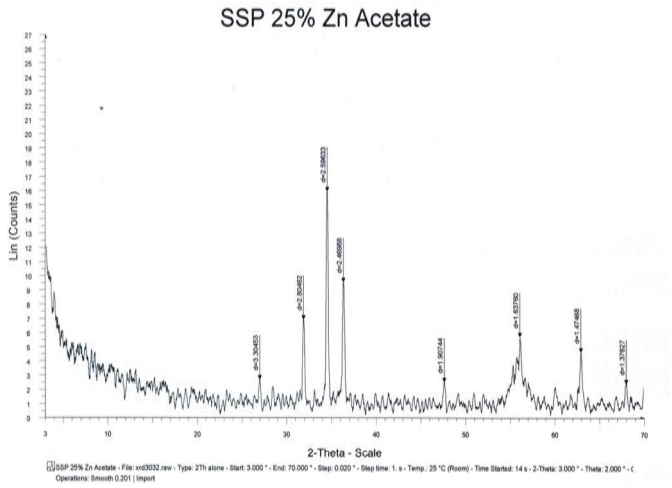
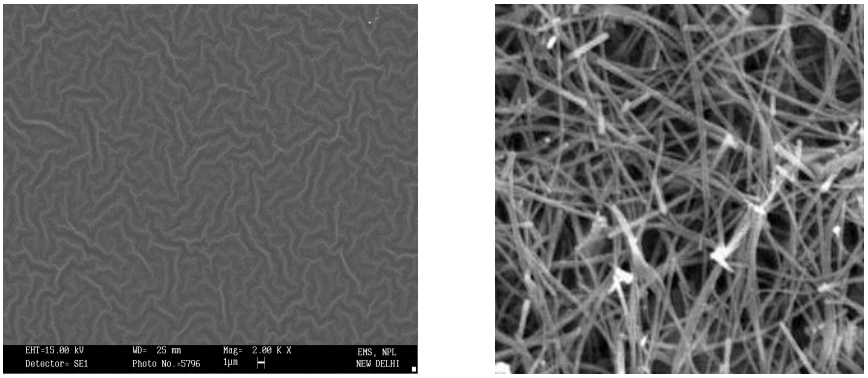


Fig. 1 *– XRD pattern of* 25% *sol concentration* ZnO *thin film nanorods*

Scanning electron micrographs (SEM) of these ZnO films on p-type Si wafer are given in Fig. 2(a, b).



(a) (b)

Fig. 2 *– SEM of* ZnO *nanowalls* (*a*) *and* ZnO *nanorods* (*b*)

confirms that broadening and asymmetry in E_2 (high) mode is due to spatial confinement of optical phonons. This phonon confinement is based on the finite correlation length of a propagating phononMultiphonon bands of these modes were also obtained and tentatively assigned. B_2 Raman inactive mode appeared at 275.46 cm^{-1} due to lowering of site symmetry. This confirmed the existence of built in electric field in the crystallites of ZnO, which induced the activity of B_2 mode. The weak bands at 516.78 and 467.56 cm^{-1} are observed due to highly localized modes near the grain boundaries having electric field within the grains close to grain boundary. Stresses in the films are evaluated from the shift in E_2 mode from the bulk ZnO E_2 mode.

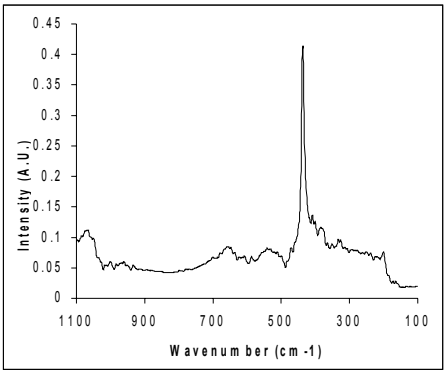


Fig. 3 – *Raman spectrum of* 5 % *sol derived* ZnO *nanowalls*

4. CONCLUSION

Nanocrystalline ZnO thin films in nanowalls and nanorods have been deposited on p-type silicon substrate by sol-gel spin coating process by using 5 % and 25 % sol concentration respectively. The structural, morphological and phonon properties revealed the formation of preferentially oriented (002) uniform nanostructured ZnO films. The single and multiphonon bands are observed in both the films Raman spectra. The spectra shift, broadening and asymmetry of optical phonons in these two different nanostructures reveals the spatial confinement of phonons. Stress in the films is calculated from the shift in E_2 mode position.

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