Correlation of Raman and X-Ray Diffraction Measurements of Annealed Pulsed Laser Deposited ZnO Thin Films

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Raman spectroscopy, x-ray diffractometry and atomic force microscopy have been used to characterize ZnO thin films grown by pulsed laser deposition as a function of the post-growth annealing temperature. The results show substantial enhancement and broadening of certain Raman features which correlate excellently with the change in width of the x-ray diffraction peaks. The 570cm^{-1} Raman feature showed pronounced asymmetry and enhanced intensity in the unannealed sample. An increase in grain size observed after subsequent annealing produced a substantial reduction in both the asymmetry and intensity of this peak. Our experimental data suggest that electric fields, due to charge trapping at grain boundaries, in conjunction with localised and surface phonon modes are the cause of the intensity enhancement and asymmetry of this feature.

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Introduction

Recent years have seen a renewed interest in the II–VI semiconductor ZnO (direct bandgap ~3.3 eV). ZnO crystallises in the wurzite lattice, is optically transparent with a large exciton binding energy of 60 meV, and is capable of UV emission and lasing. ZnO is normally n-type, but p-type ZnO has been grown which has contributed significantly to the fabrication of UV / blue LED's and laser diodes. Recently ZnO nanowires have shown UV lasing under optical pumping, and fabrication of a homostructural ZnO p-n junction has been reported [see e.g. ref. 1-3].

In this study Raman Spectroscopy and x-ray diffraction (XRD) were employed to characterise thin films grown using pulsed laser deposition (PLD) and annealed in situ at various temperatures. Our data allow us to firmly identify the mechanism responsible for enhancement of the 570 cm^{-1} Raman feature observed in polycrystalline samples.

Experimental Details

ZnO films were grown on (0001) sapphire substrates by PLD using a 10 Hz pulsed KrF excimer laser (λ=248 nm). The fluence on target was set at 1.7 J/cm^2 for all samples. A ZnO ceramic target (99.99%) was used throughout. The target to substrate distance was ~ 4 cm. The thin films were grown in an O_2 (purity 99.99%) pressure of 0.3 mbar and the substrate temperature was maintained at 400°C during growth. Typically the films were

150-200 nm, giving a deposition rate of 0.025nm/pulse. The films were subsequently annealed in O_2 (0.3 mbar) between 400°C and 600°C (see Table 1) in the growth chamber immediately after deposition. SEM data show that the films are continuous and show no evidence of porosity. The crystal structure and quality of the samples were investigated by XRD in the θ-2θ mode (Siemens D500 using Cu K_α radiation). Raman scattering measurements were performed using a micro-Raman spectrometer equipped with a CCD detector. Raman spectra were excited with 1.96 eV photons from a He-Ne laser (λ~632 nm) or, for the resonance excitation measurements, with 3.82 eV photons from a UV laser (λ=325 nm), in both cases using back scattering geometry. The He-Ne laser beam of 5-6 mW was focussed on the sample surface to a spot of diameter ~ 10 μm. Atomic force microscopy (AFM) measurements were made using a commercial AFM in contact mode operation.

Results

X-ray diffraction measurements as a function of annealing temperature are presented in figure 1. They are dominated by the (0002) and (0004) ZnO peaks along with the prominent (0006) sapphire peak. The dominance of the (0002) and (0004) peaks indicates that ZnO thin films highly textured along the (0001) direction have been grown [4]. The lattice parameters of the ZnO thin films perpendicular to the substrate can be calculated from the diffraction angles corresponding to the ($10\bar{1}0$) and (0002) planes. The intensity of the $10\bar{1}0$ peak is small compared to the (0002) peak intensity due to the high degree of c-axis orientation. The average values of c- and a-axis lattice constants of our PLD samples are 0.518 nm and 0.330 nm respectively and the values for all samples were identical within the limits of our experimental accuracy (± 0.001 nm). The average grain size (parallel to the (0002) direction) of the ZnO films can be estimated from the full width at half maximum (FWHM) of the (0002) peak using Scherrer's relation [5] (see Table 1). The range of annealing temperatures used in our work coincides with those known to lead to major grain growth [6-7]. The annealed samples show a decrease of (0002) peak FWHM and consequent increase in grain size with increasing annealing temperature. These results are supported by AFM imaging of the samples (figure 2), where measurements of the lateral grain sizes are 135 ± 40 nm for the sample annealed at 400^0C and 180 ± 50 nm for the sample annealed at 500^0C. The annealing process clearly produces a recovery of the crystal structure and increase of the grain size. We note that in our experimental conditions, the increase in grain size is achieved after annealing for relatively short times. Such an effect was also observed in the case of magnetron sputtered ZnO [8].

The unpolarized Raman spectra (with He-Ne excitation) of the ZnO thin films are shown in figure 3 as a function of annealing temperature. The peaks at 418 cm^{-1} and 751 cm^{-1} are due to scattering from the sapphire substrate. The E_2 437cm^{-1} peak, characteristic of the wurtzite lattice, can be seen in all samples. The A_1(TO) mode at 379 cm^{-1} is apparent in samples c and d. However, the Raman spectra are dominated by the longitudinal optical vibration at ~570cm^{-1}. This band is attributed to the E_1(LO) mode [9]. The intensity and FWHM of the 570 cm^{-1} peak appears anomalously high for the unannealed sample and the sample (b) which was annealed at 400^0C, but it is reduced dramatically (by a factor of ~100 relative to the sapphire features) with increasing annealing temperature. In addition, this feature shows a marked asymmetry which also decreases with increasing annealing temperature. Raman spectra were also measured with UV excitation λ=325 nm (or 3.82eV) and are shown in figure 4. The spectra from all the samples are similar, that is the strong band at 570 cm^{-1} was observed below the 800 cm^{-1} spectral region whereas a 2LO vibrational mode at ~1150 cm^{-1} was recorded in the higher spectral range as reported by several authors [10-11]. The Raman peak at 570 cm^{-1} is symmetric for all the PLD-grown ZnO samples when the excitation is at or above resonance.

Discussion

We observe a clear correlation between the XRD data and the corresponding non-resonant Raman spectra as a function of annealing temperature. As the average grain size increases, we observe a reduction in the relative intensity and asymmetry of the 570 cm^{-1} band in the Raman spectra. The intensity and asymmetry of the LO mode at 570cm^{-1} has been widely discussed in the literature. Explanations for this structure include resonance enhancement due to impurity levels in the band gap [12], contributions from both the A_1 (LO) and E_1 (LO) modes due to random crystallite orientation [12] or a combination of electric field induced (EFI) Raman enhancement and one of the following mechanisms (i) coupled phonon-plasmon scattering or (ii) localised interface and/or surface phonon modes [13].

The absence of the characteristic 2nd, 3rd order scattering in our spectra rules out the resonant enhancement by levels in the gap. These are observed in the spectra of the samples under UV excitation as expected. Contributions from both the A_1 (LO) and E_1 (LO) modes due to random crystallite orientation can also be ruled out for the reasons given by Exarhos and Sharma [12], namely that, after annealing the XRD results remain essentially the same, except for a reduction in the FWHM of the peaks, with no evidence for substantial crystallite reorientation. In addition this cannot explain the abnormally high intensity of the 570 cm^{-1} band in samples (a) and (b) in particular. Phonon-plasmon coupling is known to produce significant line shifts and broadening in Raman spectra. However, for highly polycrystalline material, the contribution of the lower frequency L^- mode is generally absent, and a shift and broadening to higher energy of the L^+ mode is observed. This behaviour is not seen in our samples, hence we believe that the line broadening we observe is unlikely to be due to phonon-plasmon coupling.

The most consistent explanation of the behaviour of our Raman data is in terms of EFI enhancement (via charge trapping at grain boundaries) of the $570cm^{-1}$ feature [13]. This enhancement effect in conjunction with the presence of localised/surface phonon modes, which arise due to the small grain size, accounts for both the intensity and asymmetry of the peak in the unannealed sample [13]. Surface phonon modes have been reported at $\sim 550cm^{-1}$ in ZnO [14], which is close to the low energy side of the broad LO mode. In the annealed samples, the increase in the grain size reduces the grain boundary density and hence the effects of charge trapping at grain boundaries. Consequently the EFI enhancement is substantially reduced, in addition to elimination of the surface/interface modes. The importance of band bending at grain boundaries in polycrystalline samples and the presence of strong electric fields has also been found in studies of varistor action in ZnO [15] and of the green luminescence mechanism [16]. Similar enhancement and asymmetry effects have also been observed in the Raman scattering of ZnO containing gold colloids [17]. These were attributed to a surface enhancement effect caused by anomalously large electric fields due to the colloid plasmon resonance. Thus, our data appear to support the model proposed in ref. [13]. This suggests that the enhancement and asymmetry of the 570cm^{-1} Raman feature of polycrystalline ZnO constitutes a good indicator of the grain size of the material.

Conclusion

Pulsed laser deposited ZnO thin films have been characterized using x-ray diffractometry and Raman spectroscopy. All films show dominant c-axis orientation. The evolution of the FWHM of the XRD (0002) peaks with annealing temperature indicates an increase in the polycrystalline grain size which is confirmed by AFM measurements. A strong correlation between the enhancement and asymmetry of the 570cm^{-1} Raman mode and the FWHM of the XRD data has been observed. The presence of electric fields, due to charge trapping at grain boundaries, in addition to localised and surface phonon modes explains the intensity enhancement and asymmetry of the LO mode in the unannealed sample. An increase in the grain size and reduction in the electric field intensity due to annealing lead to a decrease in the intensity and asymmetry of the LO mode.

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Tables:

Table 1:

Growth conditions and results of x-ray analysis for our PLD-grown ZnO thin films.

Sample	Annealing temp. (^oC)	Annealing time (min)	FWHM of (0002) peak (^{o})	Average grain size (nm)
a	No anneal	-	0.34	32
b	400	10	0.22	67
c	500	15	0.21	79
d	600	10	0.20	81

Figure Captions:

Figure 1:

θ-2θ XRD scans showing the (0002) and (0004) Bragg peaks obtained with the PLD-grown ZnO films : (a) unannealed; (b), (c) and (d) annealed at 400°C, 500°C and 600°C respectively.

Figure 2:

AFM images of PLD-grown ZnO thin films: (a) annealed at 400^0C; (b) annealed at 500^0C. The average grain sizes estimated from these images are 135 ± 40 nm for the sample annealed at 400^0C and 180 ± 50 nm for the sample annealed at 500^0C.

Figure 3:

Non-resonant (λ_{exc} = 632 nm) Raman spectra of PLD grown ZnO thin films : (a) not annealed; (b), (c) and (d) annealed at 400°C, 500°C and 600°C respectively.

Figure 4:

Resonant (λ_{exc} = 325 nm) Raman spectra of PLD grown ZnO thin films : (a) not annealed and (c) annealed at 500°C. Similar spectra were obtained for the other samples. The 2LO feature characteristic of resonant Raman spectra is clearly seen at ~ 1150 cm^{-1}.

Figure 1:

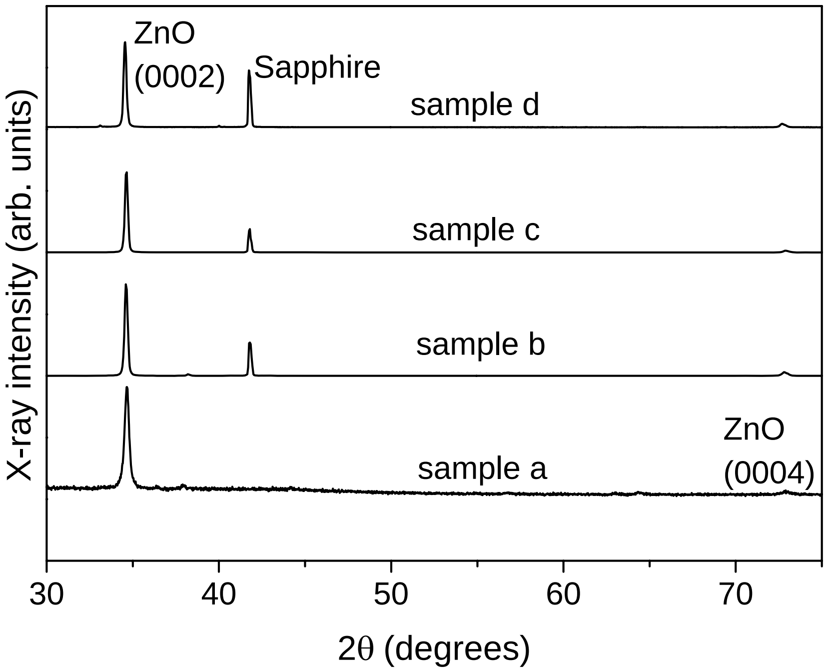

ZnO
(0002)
Sapphire
sample d
sample c
sample b
sample a
ZnO
(0004)
X-ray intensity (arb. units)
30
40
50
60
70
2θ (degrees)

Figure 2:

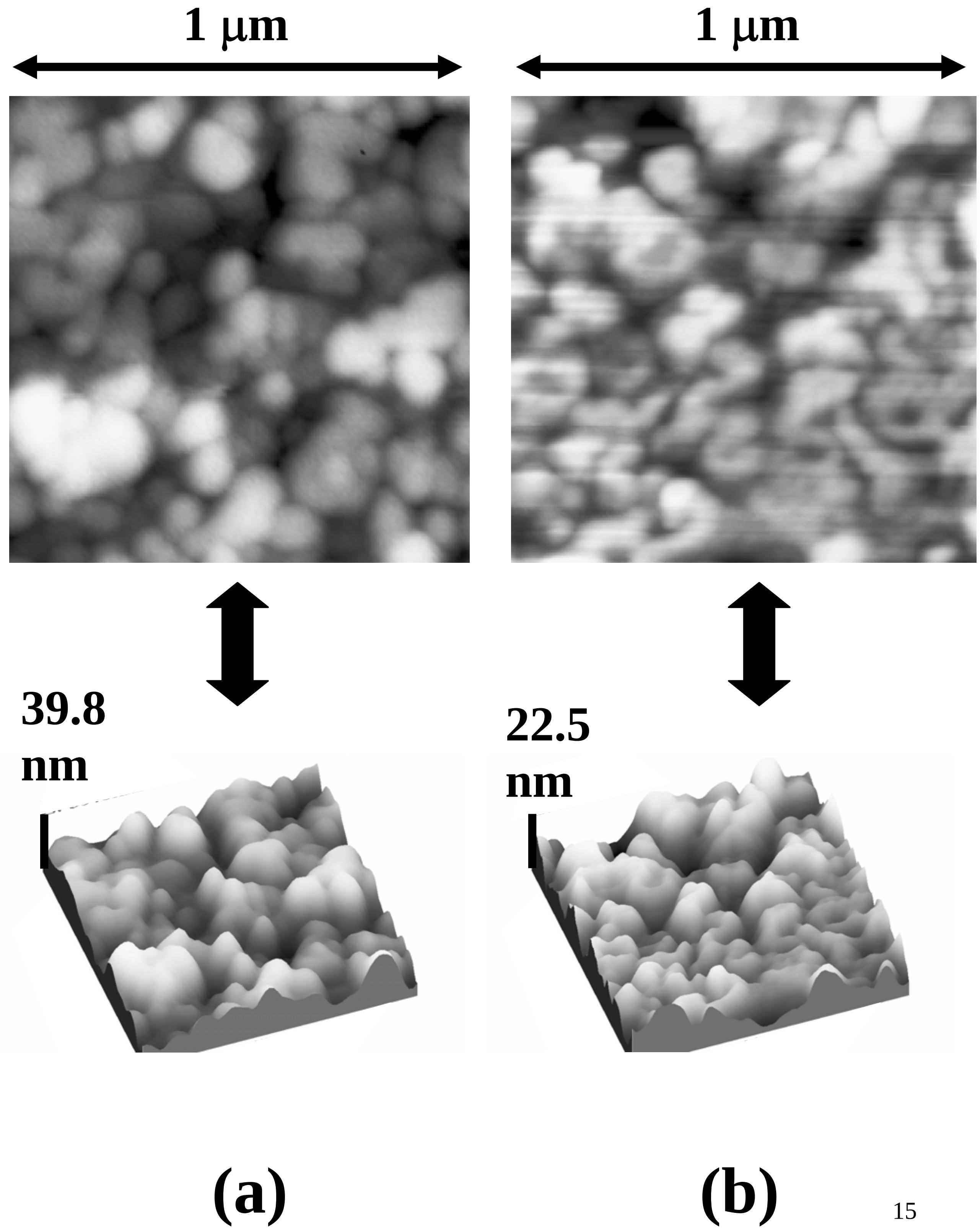


Figure 3:

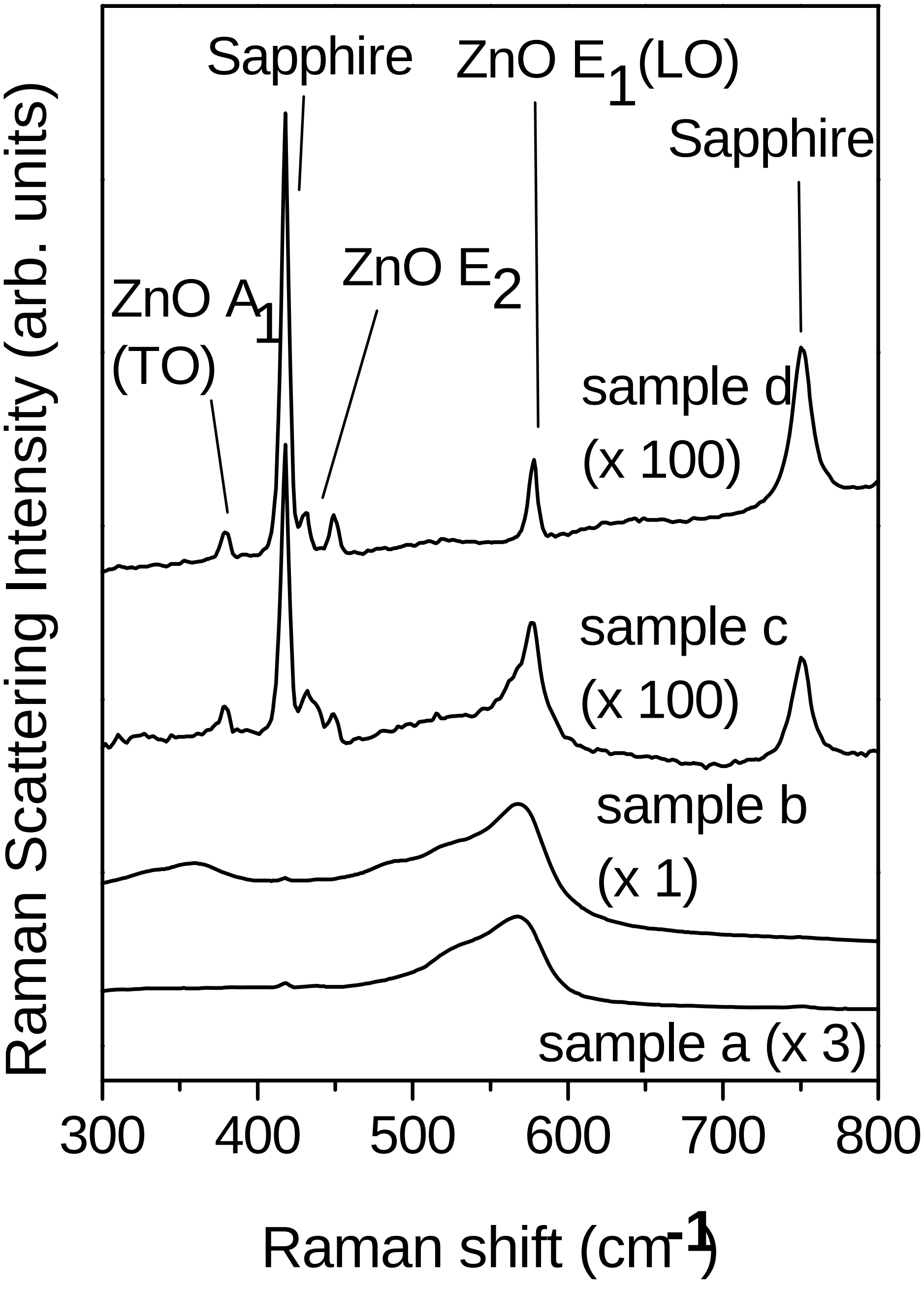
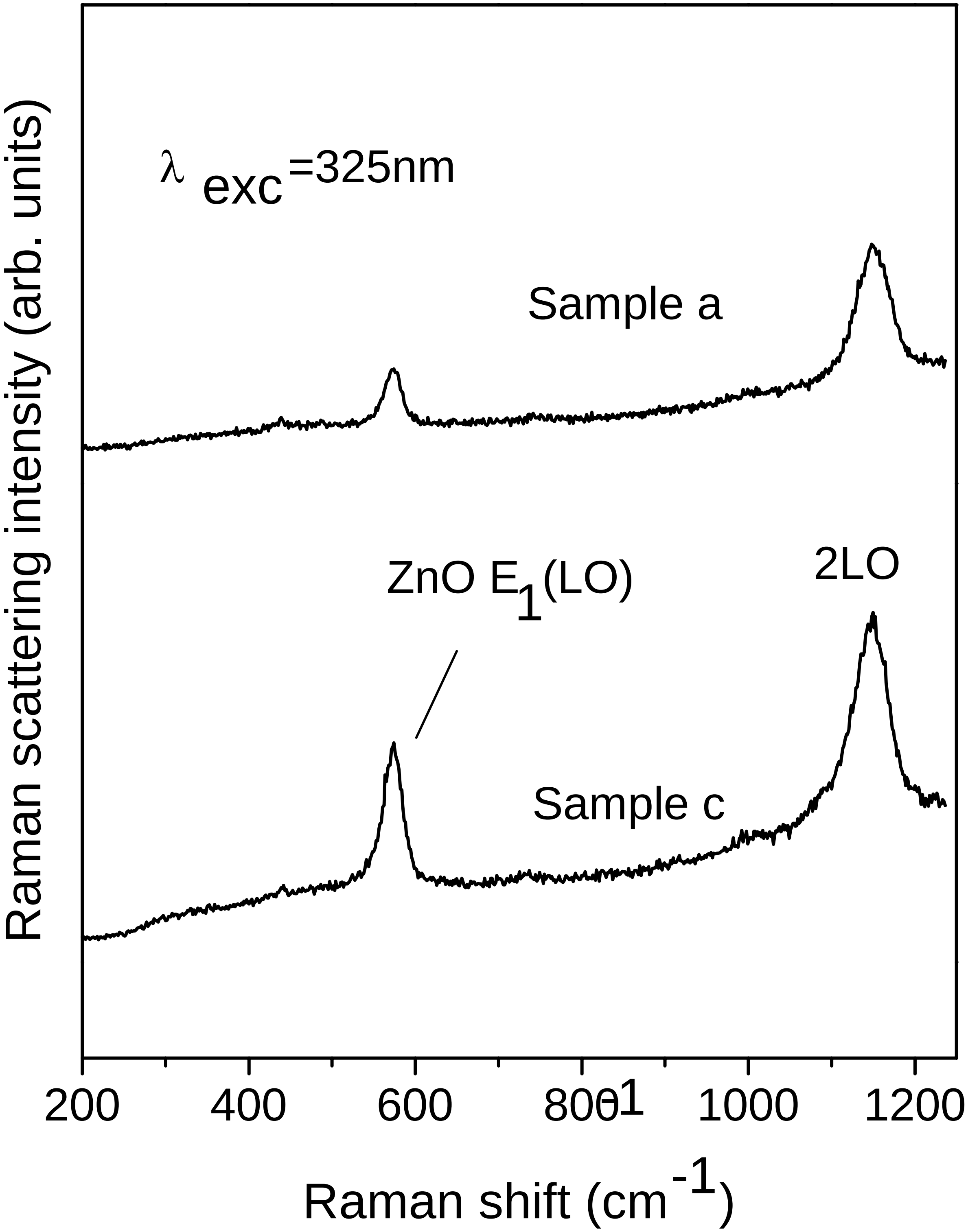

Sapphire
ZnO E1(LO)
Sapphire
ZnO E2
ZnO A1
(TO)
sample d
(x 100)
sample c
(x 100)
sample b
(x 1)
sample a (x 3)
Raman Scattering Intensity (arb. units)
300
400
500
600
700
800
Raman shift (cm-1)

Figure 4:


λ exc =325nm
Sample a
ZnO E1(LO)
2LO
Sample c
Raman scattering intensity (arb. units)
200
400
600
800
1000
1200
-1
Raman shift (cm-1)