Film Thickness Controlled Photo-luminescence Emission in ZnO:Si Nano-composites

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Abstract

As grown ZnO:Si nanocomposite films fabricated by thermal evaporation showed broad photoluminescence (PL) spectra due to merging of four prominent peaks viz 370, 410, 470 and 520 nm. Investigations revealed the role of interface in contributing to the two blue peaks at 410 and 470 nm. While the 470 nm is found to vary with ZnO grain size and their density, the 410 nm peak is attributed to the volume of shell surrounding ZnO nanoparticles. This study shows the contribution of ZnO cluster size and their density, as influenced by film thickness, in the PL spectra of the samples.

Keywords Nano-composites, Nanostructures, Photoluminescence, Oxides

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1 Introduction

Zinc Oxide (ZnO) is a II-VI wide band gap semiconductor ($E_g = 3.2$ eV) that has attracted attention for its light emitting properties [1]. However, due to lack of prominent emission in the red wavelength and 400-500 nm region, attention had been focussed on the fabrication of ZnO:Si nanocomposites with sol gel, rf sputtering and via chemical routes where porous-silicon or nano-silicon is expected to contribute emissions in red region [1]. While these attempts have had some success they present tedium fabrication process. Hence, we adopted simple thermal evaporation method to achieve similar results. Our preliminary analysis [2] and thereafter improvement in the properties on annealing [3], showed the potential of thermal evaporation. In the present work, we have investigated the role of film thickness on the photoluminescence emissions. Variation in the grain size, defects within the grains and interfacial regions can be expected with film thickness. Consequently, these changes would get reflected in the photoluminescent property of the ZnO:Si nanocomposite film.

Pelletized mixture of powdered ZnO and n-silicon mixed in a ratio of 1:2 by weight was used as the starting material for fabricating ZnO:Si nanocomposites films. The method of fabrication of films has been described elsewhere and therein have explained merits of selecting the 1:2 ratio [2]-[5]. Thickness of the films were controlled with the help of a quartz digital thickness monitor (DTM-106). All the depositions were made on microscopy glass substrates maintained at room temperature. Samples fabricated with ZnO:Si compositional ratio of 1:2 of thickness 60, 90, 120, 150 and 180 nm are referred to as (c60), (c90), (c120), (c150) in order to identify the samples. The structural studies were done using Philips PW3020 X-Ray Diffractometer (XRD). Photoluminescence (PL) scans were recorded on Fluorolog Jobin Yvon spectroscope (Model 3-11) using an excitation wavelength of 270 nm. Renishaw’s “Invia Reflex” Raman spectroscope was used for measurements using Ar$^+$ laser.

2 Results and Discussion

Figure 1 compares the PL behavior of three different thickness nanocomposite films of ZnO:Si grown with 1:2 mass ratio starting material. A huge second harmonic peak at 540 nm is seen since the spectra were recorded without the use of filters. The region between 280-520 nm clearly shows variation in PL emission with film thickness, however, all the samples have four common peaks, namely at 370, 410, 470, 520 nm. The peaks at 370 and 520 nm are attributed to transitions across the ZnO band-gap and between conduction energy level and energy level introduced by Oxygen vacancy defects occurring within the ZnO grains respectively. However, the peaks at 410 and 470 nm are relatively a new entrant with recent works attributing it to the heterogeneous boundaries [3]-[6].

The contribution from 370 and 520 nm peaks were found to vary with film thickness (see fig 2). While the contribution of the 370 nm peak decreases with film thickness that from the 520 nm shows an exponential
increase. The nature of curves in fig 2 suggests that the defects increase in ZnO grains with film thickness and conversely the perfect wurtzite crystal structure decreases. Earlier works have shown that existence of comparable contribution of 370 and 520 nm and in turn amount of lattice with and without defects is a crucial factor to obtain broadening in PL spectra [4, 5]. The region of intersection of the two curves of fig 2 namely the range 60-90 nm, marks the sample thickness that would potentially give broad emissions (here sample ‘c60’, see fig 1). Thus the film thickness would play a crucial role in the optical properties of these nanocomposite films. We believe that this influence should be manifesting itself as variation in ZnO grain size. We now discuss the structural analyses which should throw light on our assumption about role of grain size.

Fig 3 shows Raman spectra recorded for sample ‘c60’, ‘c120’ and ‘c150’. Three prominent peaks are seen at 310, 430 and 570 cm\(^{-1}\), consistent with our earlier reports [2]. While 430 cm\(^{-1}\) is the unresolved peak of wurtzite ZnO structure and amorphous silicon, the peak position at \(\sim 570\) cm\(^{-1}\) corresponds to the defect related mode of ZnO grains. The third peak at \(\sim 310\) cm\(^{-1}\) is associated with the LA mode of amorphous silicon [2, 3]. The variation of the 310 cm\(^{-1}\) Raman peak with film thickness is shown in fig 4(A). The linear increase in this peak’s contribution with thickness indicates that for the given ratio of starting material, the amount of silicon (as compared to ZnO) increases in the thicker films. This would imply ‘N’, the cluster density of ZnO decreases with increasing film thickness. Since the 430 cm\(^{-1}\) Raman peak is an unresolved peak from

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**Figure 2:** Variation of percentage contribution of PL emissions of 370 nm and 520 nm with thickness.

**Figure 3:** Raman Spectra of as grown samples ‘c60’, ‘c120’ and ‘c150’.
Figure 4: Variation with film thickness, the contributions of (A) 310 cm$^{-1}$, (B) wurtzite structured ZnO and (C) Defects related 570 cm$^{-1}$ Raman peak.

amorphous silicon and wurtzite structured ZnO, an estimation of variation in wurtzite structured ZnO with film thickness would require the subtraction of contribution from amorphous silicon (area of 310 cm$^{-1}$). The net area of the 430 cm$^{-1}$ Raman peak can be thought to be a linear sum being contributed by amorphous silicon and wurtzite and can be expressed as

$$\Delta_{430} = a\Delta_{ZnO} + b\Delta_{310}$$

As a first approximation we can assume $a=b=1$. Fig 4(B) and (C) shows variation in contribution from wurtzite (peak area $\Delta_{430} - \Delta_{310}$) and defects ($\Delta_{570}$) with thickness. These plots(109,153),(889,898) have only three points due to the inability in deconvoluting broad peaks due to the lack of prominent shoulders in the spectra. The wurtzite contribution decreases with thickness in agreement with fig 2 (see fig 4 B). As reported earlier, [2, 3], samples with comparable amount of wurtzite and defects give broadening. Since we are comparing samples of different thickness, making inferences from the above data is difficult. However relative wurtzite and defect presence with film thickness was calculated using the best fit lines of Fig 4(B) and 4(C). Figure 5 shows that the ratio of ($\Delta_{430} - \Delta_{310}$)/$\Delta_{570}$ decreases with increasing thickness. In short, our Raman data shows that the density (N) of ZnO clusters are decreasing and within them, the lattices with wurtzite structure diminishes more rapidly than those with defects. This explains why there is a stronger 520 nm peak in PL as compared to the 370 nm peak in thicker samples.

For thicker films, X-ray diffractograms exhibit a lone peak at $2\theta = 36^\circ$ that too only in samples ‘c90-c150’ (Fig 6). This peak is associated with the (101) peak of ZnO (ASTM Card No. 36-1451). Interestingly the Zinc Oxide peak is absent in ‘c60’ and ‘c180’. The absence of peak in ‘c60’ has been consistently observed in very thin samples of our studies [2, 3]. Contribution of amorphous silicon is seen to increase with thickness from fig 4(A), implying ‘c180’ films though thicker have low grain density of ZnO, and hence possibly explains the lack of strong diffraction peaks.

To understand how film thickness contributes and manifests itself on the optical properties of our sample we calculate the size of ZnO grains from the 36$^\circ$ XRD peak. Calculations are done using standard Debye-Scherrer formula given by eqn

$$g = \frac{0.9\lambda}{\beta \cos \theta}$$

where ‘$\beta$’ is full width at half the maximum intensity (FWHM) of the peak [7]. The grain size was found to increase with film thickness (Table I). Viewed in conjunction with results of Raman spectra we may state that with increasing film thickness, the population of ZnO grains decreases while their size increases. The volume of these larger grains enclose higher number of ZnO lattices with defects as compared to those with perfect wurtzite structure.
Figure 5: Relative presence of wurtzite structured ZnO to defects incorporated ZnO ($\Delta_{430} - \Delta_{310}/\Delta_{570}$) for varying thickness of the film.

Table 1: Variation of ZnO grain size with thickness of the film.

| Thickness (in nm) | Grain Size (in nm) |
|------------------|--------------------|
| 90               | 7                  |
| 120              | 18                 |
| 150              | 11                 |

We now discuss the two (PL) peaks observed in the blue region, at 410 and 470 nm. In our previous reports, we had shown a linear trend between $\Delta_{470}$ (area enclosed by the 470 nm peak) and $R^2N$ [3]. The grain density ‘N’ in our previous study was found to be proportional to the amount of ZnO present in the starting material. However, here the compositional ratio of the starting material is fixed and hence variation in ‘N’ is co-related to film thickness. Basically, the variation in contribution of the 470 nm PL peak ($\Delta_{470}$) can be seen as a mathematical problem, with it having a functional dependence on grain size (R) and number of grains (N). In terms of partial differential equation, we write

$$
\frac{d\Delta}{d\tau} = \frac{\partial \Delta}{\partial R} \frac{\partial R}{\partial \tau} d\tau + \frac{\partial \Delta}{\partial N} \frac{\partial N}{\partial \tau} d\tau
$$

$$
\frac{d\Delta}{d\tau} = \frac{\partial \Delta}{\partial R} \frac{\partial R}{\partial \tau} + \frac{\partial \Delta}{\partial N} \frac{\partial N}{\partial \tau}
$$

where $\tau$ is the film thickness. Table I and fig 4(A & B) show that $\frac{\partial R}{\partial \tau}$ and $\frac{\partial N}{\partial \tau}$ have opposite signs with $\frac{\partial N}{\partial \tau}$ being negative. A plot of variation in 470 nm PL peak contribution with respect to thickness (fig 7) shows a decreasing trend, suggesting the dominant influence of ‘N’ over $R^2$.

Figure 7 shows the variation in area of 470 and 410 nm PL peaks with film thickness. Both peaks show a linear relationship with the contribution of 470 nm and 410 nm peaks decrease with increasing thickness. Though the trends are similar the physics of the 410 nm PL peak is different from that of the 470 nm PL peak. The 410 nm emission is believed to result on account of a shell (it’s volume) formed by Zn-Si-O linkage bonds around the ZnO core [5, 6]. The more there are grains, the larger is the contribution from the shells.
Consequently the 410 nm is predominantly co-related to the grain density. However, a weak influence on the size of the grains can be expected. Figure 8 shows the TEM micrograph of ‘c150’ which shows a shell encircling dense ZnO core embedded in amorphous background. The shell region around a dense core is visible. Core size as calculated from TEM and XRD are fairly in good agreement with each other. While we are able to identify the contributors of emission in blue region, the mechanism of emission is still speculated and needs more investigation.

Revisiting the graph shown in figure 7 suggests that the comparable contributions of the two blue peaks can be achieved at the intersection of the best fit line for the two peaks. The intersection point is observed at a film thickness of \( \sim 60 \, \text{nm} \). Interestingly, the relative contribution of 370 nm and 520 nm peaks of PL also intersect at a thickness \( \sim 90 \, \text{nm} \).

From the previous section it became clear that the broadening effect of 370 and 520 nm of PL is largely related to the nature of ZnO grains namely relative presence of lattice with defects and those with perfect wurtzite structure. These two peaks typically do not show dependence on grain size, however our analysis suggests for the conditions in which our samples were fabricated, thicker films have lower grain density abid larger grains with and more defects. Thus, larger grains are more prone to contain defects, obliquely introducing a grain size dependancy.

The 410 and 470 nm PL peaks similarly show grain size dependancy based on the idea that smaller grains give larger grain population \( (N) \). With better control over film growth parameters, an optimum condition could be obtained. For the condition of film fabrication in this study we find best results are obtained for 60 nm thick films. While the density of grains \( (N) \) in a fabricated film cannot be changed due to the clusters being embedded in an isolating matrix, the shell and the defect concentration can be altered by post deposition annealing, as suggested in our recent work.

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Figure 6: XRD scans of as grown sample c60, c90, c120, c150 and c180.
Figure 7: Variation of percentage contribution of 470 and 410 nm PL peaks with thickness.

Figure 8: TEM image of sample ‘c150’, clearly shows the formation of a shell encircling ZnO core.

Conclusion

In summary, the PL peaks at 370, 520, 410 and 470 nm are correlated to the thickness of the thermally evaporated ZnO:Si nanocomposite films. We are successful in explaining the origin of the photoluminescence peaks at 410 and 470 nm. Though both are attributed to interface occurring at heterogeneous boundary of ZnO nanoclusters and amorphous silicon, they are different in the physics lying behind their origin. It was found that both the peaks are related to number of clusters (N) and the size of grains (R), which are strongly
influenced by the thickness of the films. The investigations indicate that whereas 410 nm comes from Zn-Si-O linkages existing in a shell around the ZnO clusters, 470 nm varies linearly with $R^2N$. Findings of the present work thus suggests that at an optimum thickness, the four PL peaks in discussion would lead to equal intensity broad-band luminescence. For the thermally grown ZnO:Si nanocomposites, the PL peaks were found to merge at a thickness of $\sim 60$ nm. We are hopeful that this study would serve as a way to monitor the interfacial region existing in nanocomposites in general and particularly be useful in tailoring the luminescence properties of ZnO:Si nanocomposites.

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References

[1] C. Jagadish and S. J. Pearton, “Zinc Oxide Bulk, Thin Films and Nanostructures, Elsevier Ltd.”, 2006.
[2] S.Siddiqui, C.R.Kant, P.Arun and N.C.Mehra. Phys. Lett. A 372 (2008) 7068.
[3] Shabnam, C.R.Kant and P.Arun. Mater. Res. Bull. 45 (2010) 13068.
[4] Shabnam, C.R.Kant and P.Arun. Size and Defect related Broadening of Photoluminescence Spectra in ZnO:Si Nanocomposite Films. communicated available at arXiv:1007.2142.
[5] Shabnam, C.R.Kant and P.Arun. White Light emission from annealed ZnO:Si Nanocomposites Thin Films. communicated available at arXiv:1101.4119.
[6] Yu-Yun Peng, Tsung-Eong Hseih and Chia-Hung Hsu, Nanotechnology, 17 (2006) 174.
[7] “Elements of X-Ray Diffraction”, B.D.Cullity (London,1959).
[8] X.Feng, X.Yuan, T.Sekiguchi, W.Lin and J.Kang, J.Phys.Chem. B, 109 (2005) 15786.
Intensity (Arb.Units)
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(c1)